Free Form Low Cost Fabrication Using Titanium
Prepared for

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THE CENTER FOR ADVANCED
MINERAL & METALLURGICAL PROCESSING
Montana Tech of the University of Montana
Butte, Montana

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Prepared for

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ABSTRACT

The Army weapons systems of the future will require improvements in transportability, maneuverability, and durability. These improvements can be realized through changes in materials of construction. Titanium-based alloys exhibit the exceptionally favorable strength-to-weight ratio, low density, as well as, superior resistance to erosion and impingement attack. It also displays outstanding resistance to a broad range of acids, alkalis, industrial chemicals, natural waters, and marine atmospheres. The current high costs associated with titanium-based alloys remain the main obstacle for widespread use as a material of construction. Although relatively high costs originate in the extraction and refining for the titanium based metal, the highest expenditures can be found in the fabrication of components. Free form fabrication is a growing technology that can be applied to weapons systems manufacturing. This technology utilizes digital information derived from 3D CAD data or data from 3D digitizing systems. Specialized software converts the 3D data into layered 2D data. This layered data is used by a variety of processes that join liquid, powder, or sheet materials to form parts comprised of plastic, metal, ceramic, or composite parts, in a layer upon layer manner. CAMP/Montana Tech has acquired a ProMetal R2, a three-dimensional printing machine, from The Ex One Company of Irwin, Pennsylvania. Titanium-based component fabrication with a three-dimensional printing machine, using of metals powders, and the layer-by-layer methodology, will result in a near-net shape component. For titanium components, the parts will then be subjected to a low-temperature binder removal followed by a high-temperature vacuum furnace sintering and completed by a hot isostatically press furnace stage. The process holds promise to reduce the fabrication costs for titanium components. This method is a more economical titanium fabrication technique when compared to current casting methods.

Varying the powder mixture-binder-sintering profile revealed that a Ti-6Al-4V powder mixed with 3.5% CIP powder, printed with the ammonium molybdate binder, and sintered for long times at high temperature 1440 °C in vacuum produces test geometries that result in high density approaching that is needed to make functional parts by 3D dimensional printing. The iron powder induces the formation of a liquid phase that enhances the densification. The sintered microstructure shows a typical acicular structure of a-titanium with no deleterious effect of Fe visible. Further studies will include sintering distortion control with the aid of Finite Element Software (FE) to simulate absorbed heat and shrinkage. Hot isostatic pressing (HIP) will be employed in an effort to bring the titanium component to 100% density

INTRODUCTION

Titanium is lightweight, strong, corrosion resistant and abundant in nature. Some significant facts and/or important benefits offered by titanium and titanium alloys illustrate the basis for the use of titanium today:

- The density of titanium is only about 60% of that of steel or nickel-base superalloys.
- The tensile strength as an alloy of titanium can be comparable to that of lower-strength marterisitic stainless and is better than that of austenitic or ferritic stainless. Alloys can have ultimate strengths comparable to iron base superalloys, such as A286, or cobalt base alloys, such as L605.

- The commercial alloys of titanium are useful at temperatures of about 538 °C to 595 °C (1000 °F to 1100 °F), dependent on composition. Some alloy systems (titanium aluminides) may have useful strengths above this temperature.
- The cost of titanium, while approximately four times that of stainless steel, is comparable to that of superalloys.
- Titanium is exceptionally corrosion resistant. It often exceeds the resistance of stainless steel in most environments, and it has outstanding corrosion resistance in the human body.
- Titanium may be forged or wrought by standard techniques.
- Titanium is castable, with investment casting the preferred method. (Investment cast titanium alloy structures have a lower cost than conventional forged/wrought fabricated titanium alloy structures.)
- Titanium may be processed by means of PM technology. (Powder may cost more, yet P/M may offer property and processing improvements as well as an overall cost-savings potential.)
- Titanium may be joined by means of fusion welding, brazing, adhesives, diffusion bonding, and fasteners.
- Titanium is formable and readily machinable, assuming reasonable care is taken. Titanium is available in a wide variety of types and forms.

Safety Considerations

- In molten form, titanium either dissolves or is contaminated by every known refractory.

- Combustibility and Explosibility (in air)
  - Titanium powders (< 200 Mesh) – ignition of dust clouds @ 630°F to 1090°F.
  - Titanium powders (< 200 Mesh) – ignition of dust layers @ 720°F to 950°F.
  - Titanium fines (< 48 Mesh) – can be ignited by an electrical spark.
  - Titanium dry ductile thin chips and fine turnings can be ignited with a match.
  - Titanium normal sized chips and turnings can burn with a Bunsen burner.
  - Titanium sponge or coarse turnings burn slowly and release large quantities of heat, but sponge fires can spread rapidly.

- Combustibility and Explosibility (in carbon dioxide)
  - Titanium powders (< 200 Mesh) – ignition of dust clouds @ approximately 1250°F.

- Combustibility and Explosibility (in nitrogen)
  - Titanium will burn vigorously @ 1470°F

- Combustibility and Explosibility (in dry chlorine)
  - Titanium will burn at room temperature.

- Combustibility and Explosibility (in red fuming nitric acid)
  - Titanium can react vigorously or even explosively in red fuming nitric acid, but this phenomenon has not observed in normal nitric acid.

- Spontaneous ignition has occurred in fine, water-soluble, oil-coated titanium chips and swarf.

- Dry titanium fines collected in cyclones have ignited spontaneously when allowed to drop freely through the air.
- Titanium sump fines will often ignite when they are dried.
- Titanium, in molten state, can cause a violently destructive explosion if water is present in any mold, pit, or depression into which the molten metal is poured or spilled. Under such circumstances, stream pressure, and exothermic chemical reaction, or a low-order hydrogen-air explosion can cause severe damage.

Titanium Fabrication

CNC Milling – As illustrated below, this process begins with a solid block of titanium that is reduced to the desired component by a computer-controlled mill. This process requires the work piece to be manually repositioned several times before completion. This process requires specialized tooling, produces a considerable amount of waste (titanium chips) and is geometrically limited in the shape of the final component.

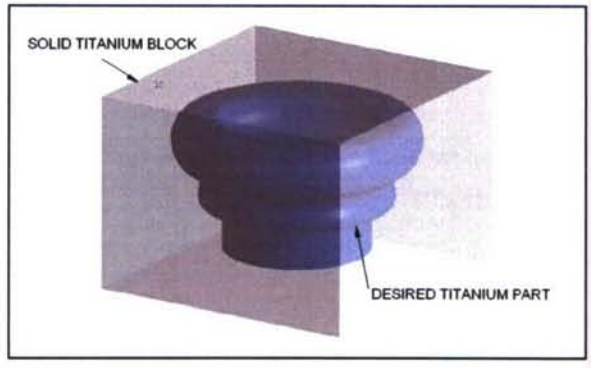

Figure 1 – CNC Milling

Investment Casting – Typically, this process begins with a wax prototype of the desired component. This wax prototype is then immersed in a liquid refractory and then dried. This cycle is repeated until the refractory shell reaches sufficient thickness. The refractory shell is then subjected to extreme heat to drive off all moisture and to remove the wax prototype. This is known as the "lost wax investment mold" process. In order to apply the investment casting process with titanium, the lost skull method for casting the molten titanium is utilized. Titanium powder or small particles of titanium sponge are introduced into a water-cooled copper crucible and subsequently melted by a plasma torch. The molten titanium that comes in contact with the water-cooled crucible will quickly solidify and become a protective layer for the molten titanium at the center or heart of the crucible. When a sufficient amount of titanium is in the molten state, the feeder is shut off and the crucible is tilted, casting the molten titanium into the refractory mold.

Centrifugal casting (rotating mold) is a method that increases the percentage of the mold filled before the titanium solidifies. This process is illustrated below.

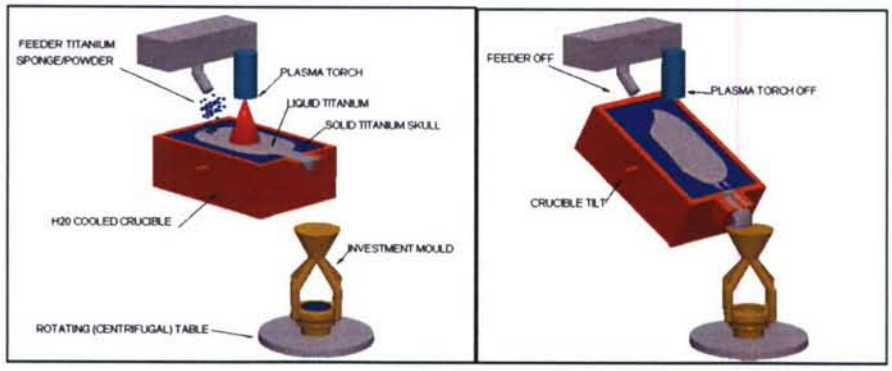

Figure 2 – Investment Casting

This process results in high energy costs, high rate of casting defects, limited geometric shape of finished part, extreme waste (skull), post manufacture cleanup of part (flashings and risers), and it is very time consuming.

Powder Metallurgy – This process also begins with the creation of a mold utilizing the lost wax process. The mold is filled with metal powders and then the mold is sealed. This sealed mold is placed into a metallic container, which is packed with refractory powders, and then a weld seals the container. The container is placed into a hot isostatic-pressing furnace (HIP) and subjected to high heat and high pressure. This process fuses the metal powders in the mold resulting in a near full density component. This process is illustrated below.

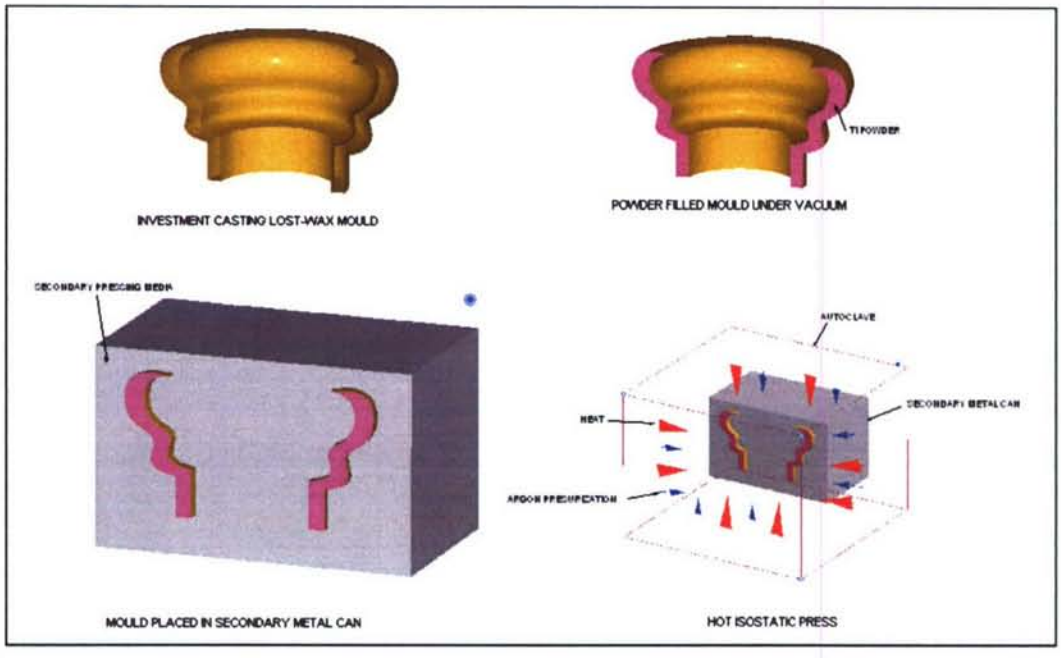

Figure 3 – Powder Metallurgy

This process results in excessive manufacturing time, high rate of defects due to poor mold filling, limited geometric shape of finished part, and post manufacture chemical cleanup of part due to refractory contamination.

Free Form Fabrication

Free form fabrication is a growing technology that can be applied to rapid manufacturing. This technology utilizes digital information derived from 3D CAD data, CT or MRI systems, or data from 3D digitizing systems. Specialized software converts the 3D data into layered 2D data. This layered data is used by a variety of processes that join liquid, powder, or sheet materials to form parts comprised of plastic, metal, ceramic, or composite parts, in a layer upon layer manner. See Appendix A for summaries of the main companies involved with free form fabrication.

FREE FORM LOW COST FABRICATION USING TITANIUM: YEAR ONE WORK PLAN

I. Infrastructure for R&D on Low-Cost Titanium Components by 3DPrinting

Task I.1a. Printing machine modification for explosion prevention

Initial meetings were held with Factory Mutual of Providence, RI, in December of 2005, for the evaluation and recommendation of design changes in the ProMetal R1 for compliance with FM safety standards. Based on the information and guidance gained from this initial meeting, a plan was devised to review the mechanical, electrical, and software alterations required to meet metal dust safety standards. Preliminary concepts involve the use of purge system to assure that titanium powders are exhausted from the build volume of the machine.

The conceptual design for the modified ProMetal R1 was completed in January of 2006. Parts were ordered and quotes were received to carry out compliance testing of the machine. These tests include:

- Radiated and Conducted Emissions
- Harmonics and Flicker
- Immunity Test for Equipment Intended for Use in Industrial Locations,
- Product Safety Testing and Investigation for laboratory and Electrical Equipment.

The sheet metal and frame parts for the modified ProMetal R1 were completed in April of 2006. These modifications can be seen in the following figures.

Figure 1 - Rear view of the modified ProMetal R1 displaying the exhaust fan outlet (upper right) and the inlet vent (center front of frame).

Figure 2 – Side view of modified ProMetal R2 frame.

Figure 4 – Modified ProMetal R1

The modified ProMetal R1 has an inlet filter near the base of the front cover, vents in the working platform, and an exhaust fan at the rear of the upper chamber. Any process gases from this system are exhausted through the facility ductwork. A rubber seal around the junction between the cover and working platform prevents filtration of any emissions into the environment. A latch on this seal prevents opening of the cover if an explosion occurs in the working chamber.

The following safety issues, related to design and manufacturing of the equipment used for 3D printing titanium powders, were identified:

- Titanium powder is pyrophoric
- Titanium powder will ignite in atmospheres of carbon dioxide, nitrogen, and oxygen
- Titanium powder has an ignition temperature of dust cloud 460 C
- Minimum ignition concentration is 0.045oz/ft^3.

It was determined that the handling and processing of titanium powder will always present the possibility of a dust cloud. Therefore, machine modifications must:

- Prevent an ignition source
- Prevent dust concentrations above ignition limit
- Maintain inert gas environment

In order to address these critical aspects, the following machine design rules were incorporated into the modified ProMetal R1:

- Prevent dust concentrations above minimum by maintaining gas flow to exhaust dust
- Prevent heat source by using non-metallic bearings and potted electrical contacts
- Maintain inert gas environment by shrouding working chamber with argon gas

Testing of the modified ProMetal R1 began in September of 2006 by Ex One Company at Concurrent Technologies Corporation (CTC) in Johnstown, Pennsylvania. The information developed in the modification of the ProMetal R1 is directly transferable to the modified ProMetal R2 platform which will be used for 3D printing of titanium powder. Similarities in method of sealing the work zone, identifying possible ignition sources and isolating them, sensing the atmosphere for the presence of

unwanted gases and software monitoring of sensors and safety devices exist between the R1 and R2 systems.

During the design phase of the modified Prometal R2, the concept of using argon as a shield gas during the 3D printing of titanium powders was re-addressed. Argon displaces oxygen and could potentially displace enough oxygen to present a breathing hazard and since the titanium powder on which the binder is be printed will not undergo a state change during this portion of the process, it was determined that the use of argon was not necessary. The build area on the modified ProMetal R2 was designed to incorporate a minimum of four air exchanges per minute. This rapid turnover of the air within the build area of the machine will suffice in removing fine particulate powder from the atmosphere, thereby negating the risk for explosion.

After communications with Ex One and Montana Tech/CAMP representatives in October of 2006, it was decided that the ProMetal R1, currently on the Montana Tech campus, would be replaced with a standard ProMetal R2 system, not capable of printing titanium, until such time as a titanium-capable ProMetal R2 is completed and installed at Montana Tech. The standard ProMetal R2 was shipped during the week of November 6, 2006 and installation was completed during the week of November 20, 2006. At that time the estimate for completion of the titanium-capable ProMetal R2 ranged from the end of February to early March 2007. The following modifications were reviewed and approved in October of 2006.

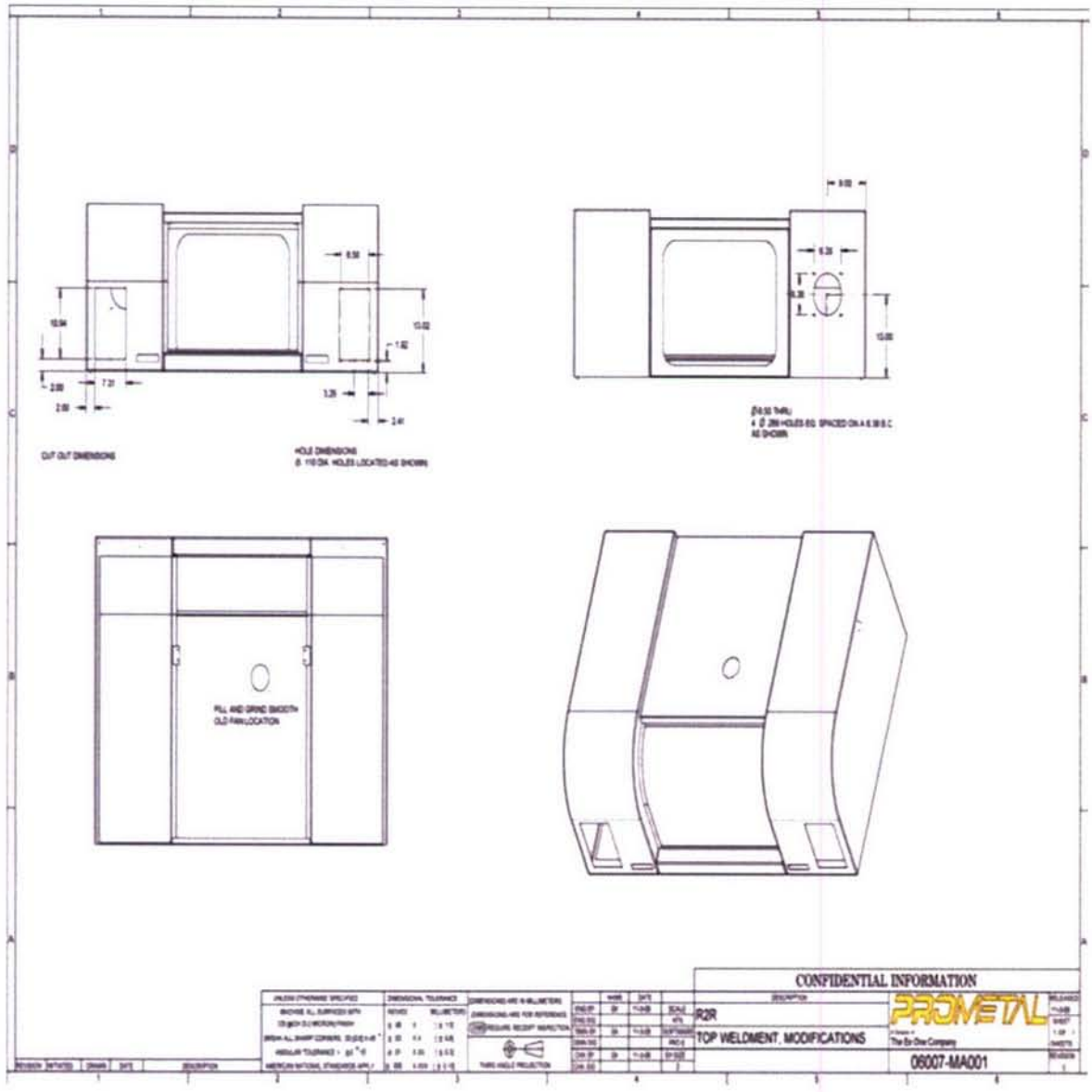

Figure 5 – Top Build Area Modifications

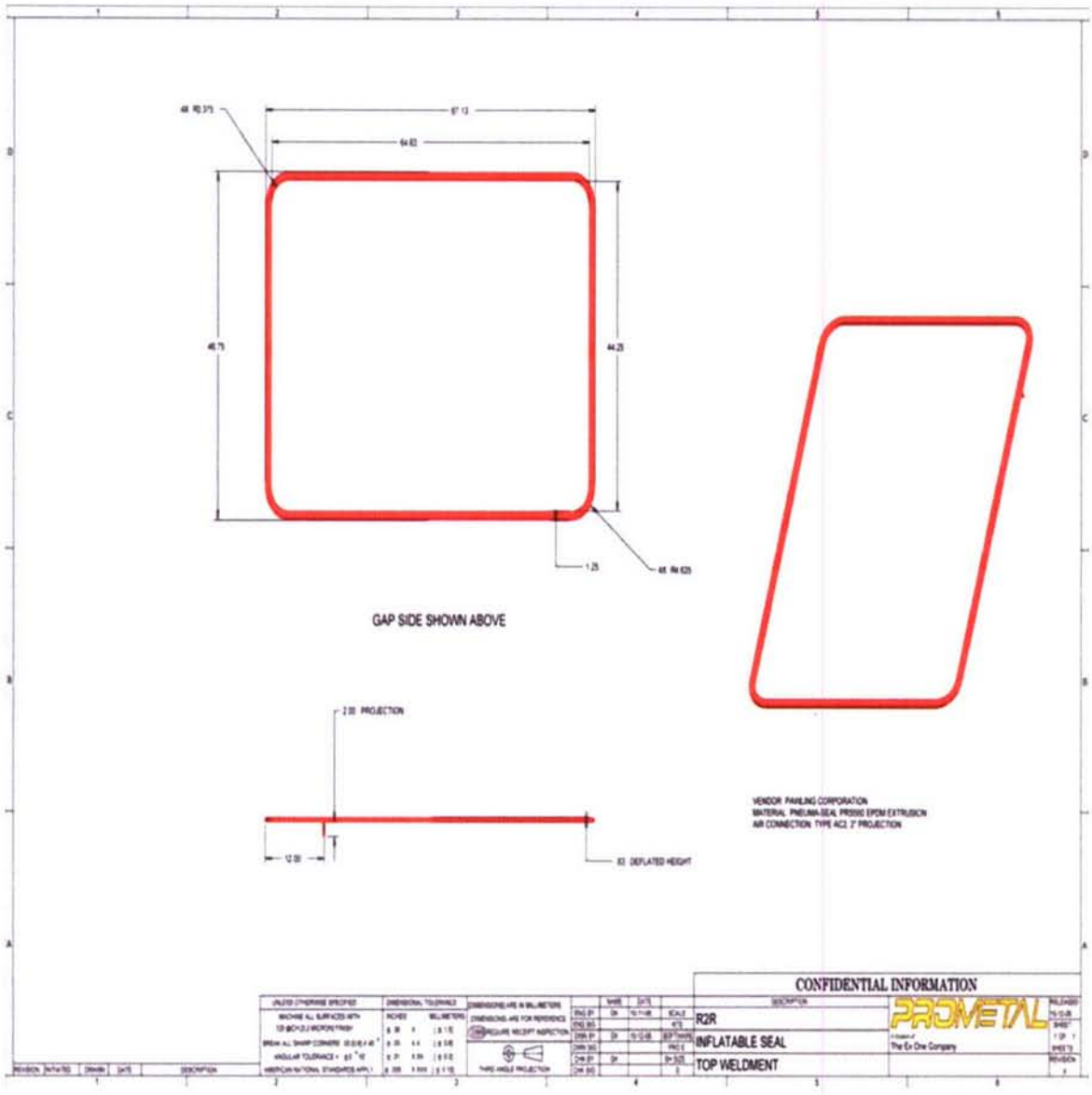

Figure 6 – Inflatable Seal for Build Area

Figure 7 – Purge System Control Module at the Ex One Company in Irwin, Pennsylvania

In November of 2006, as agreed upon between Ex One and Montana Tech/CAMP, a standard R2 was installed on the Montana Tech campus to aid Montana Tech/CAMP personnel in obtaining background knowledge in the use of three-dimensional printing equipment. During this time much of the work at Ex One was devoted to development of critical electronics specifications and packaging and the air handling system. Examples of this work can be found in the following figures:

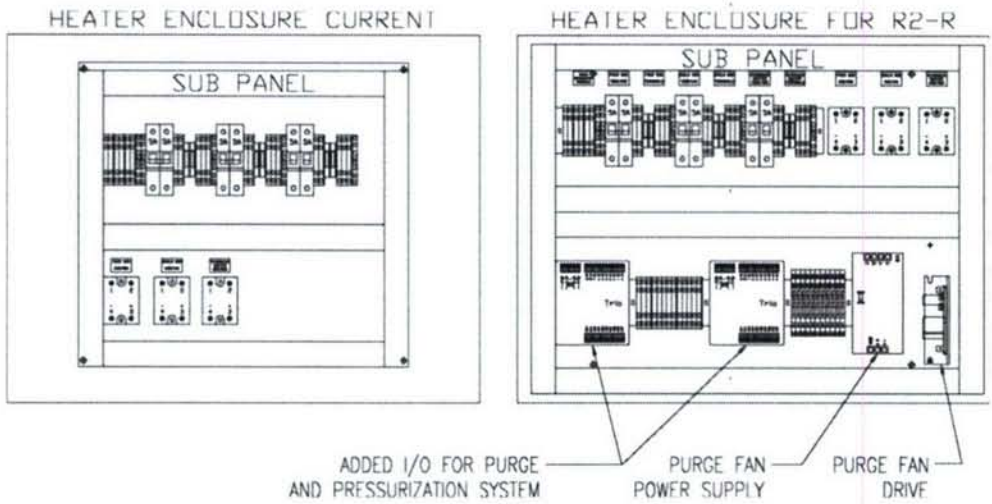

Figure 8 – Heater Enclosure Modifications

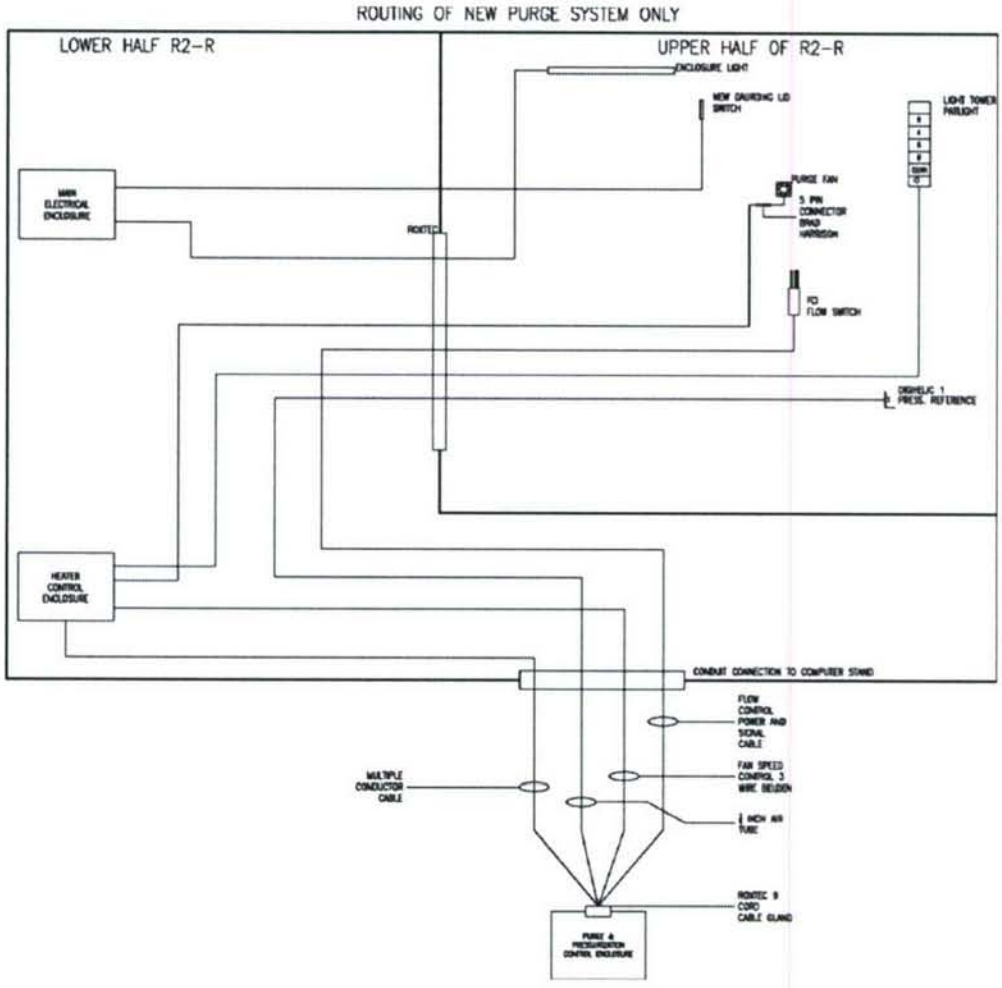

Figure 9 – Purge System Modifications

The bulk of the modified Prometal R2 fabrication took place at the Ex One Company during the month of January of 2007. The pictures included in the following figure illustrate this progress.

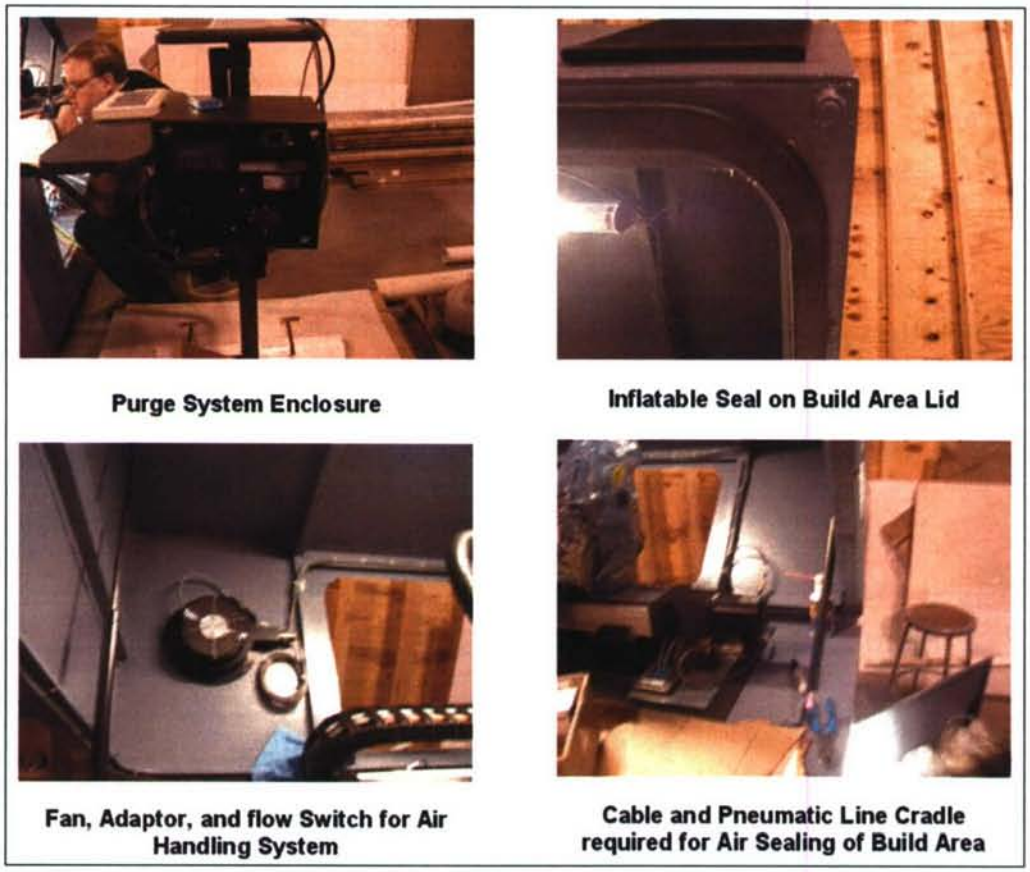

Figure 10 – ProMetal R2 Progress January 2007

Several correspondences between the Ex One Company and Montana Tech/CAMP personnel were required in February of 2007, to coordinate the modified ProMetal R2 air exhaust ducting system and the Montana Tech campus ducting system. The following figure illustrates the results of these correspondences.

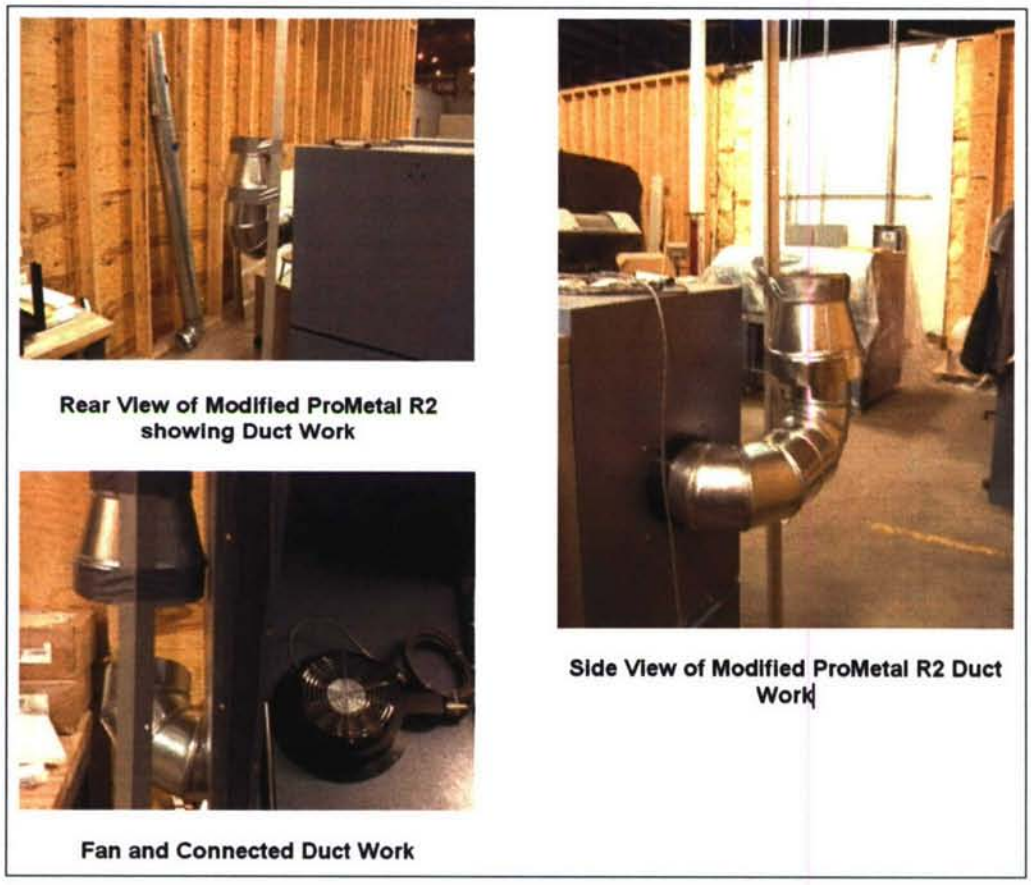

Figure 11 – Duct Work on the Modified ProMetal R2

During the month of March 2007, Ex One delivered the Titanium R2 three-dimensional printing machine to Montana Tech. The machine incorporated all safety modifications designed by Ex One engineers, with approval from Montana Tech/CAMP, and was functionally tested for all safety subsystems prior to shipment. The machine was shipped with a supply of stainless steel powder and an experimental binder, which works with stainless steel powder, but also is a likely candidate for use with titanium powders.

Task I.1b. Install printing system at Ex One

In February of 2006, personnel from the Ex One Company completed an evaluation of a laboratory near the Ex One facility, which contained safety features for operations with powder metals. The facility is operated by Concurrent Technologies Corporation (CTC) in Johnstown, Pennsylvania

By March of 2007, the Ex One Company had completed the fabrication of the modified ProMetal R1, the modified ProMetal R2 (for titanium powders), and conducted testing of all safety systems. The completed activity list for this task is as follows:

- Initial testing of modified ProMetal R1 at CTC facility

- Full scale utilization of modified ProMetal R1
- Final design of electronic components for modified ProMetal R2
- Incorporation of design elements from modified ProMetal R1 to modified ProMetal R2
- Final design of purge method, sensors and zone
- Manufacture of components for modification
- Assembly of entire modified ProMetal R2 system
- Testing of entire modified ProMetal R2 system
- Shipment of modified ProMetal R2 system to Montana Tech

Installation of modified ProMetal R2 at Montana Tech

Task I.1c. Install printing system and complete training at Montana Tech

Negotiation and execution of the End User License Agreement, between the Ex One Company and Montana Tech/CAMP, was completed In December of 2005. A ProMetal R1 Rapid Printing Machining System was shipped to Montana Tech/CAMP to be used for training purposes. This system was scheduled to be replaced with a hardened ("explosion proof") system following the design and fabrication of the modified ProMetal R2 system.

In February of 2006, the installation of a ProMetal R1 Printer at Montana Tech University was completed. The printer was located in the ELC Building, Room 103.

Figure 12 – ProMetal R2 at Montana Tech /CAMP

Actions taken to assure proper operation:

- X – Y axis perpendicularity checked and adjusted to < 0.00 1" (initial was off by 0.0 10")
- Roller flatness to build box adjusted to 0.001" (initial was off flatness by 0.002 and low 0.003)
- Sealed vent valve fitting from cap
- Replaced priming pump tubing
- Printhead function was checked and determined that all jets were working
- Installer determined that vent fans on upper cabinet are noisy and will be replaced

- Loaded Stainless Steel process settings into the system
- Printed, cured, and de-powdered test parts

The ProMetal R1 Operation Manual, which provides information on the principles of operation and contains screen shots, and the Thermal Processing white paper for Stainless Steel were provided to Montana Tech/CAMP by the Ex One Company. Then hands-on training was provided to one operator and consisted of:

- Machine overview
- Key components of the machine (mechanical, fluid, electrical, software)
- Principles of operation of the primary components
- Types of part files used by the software (STL/SLC)
- Instructions and importance of cleanliness
- Directions for safe operation
- Chemical descriptions and precautions (MSDS)
- System maintenance
- Machine Operations
- Startup instructions
- Software screen walkthrough
- Fluid system operation explained
- Motion systems described and explained
- Printhead startup - how to return missing jets to operation
- Printhead test print instructions and how to correct for missing jets
- Process parameter description and instructions for adjustment
- Principles of binder saturation
- Drop mass measurement for saturation calculation
- Part loading (rotation and scaling)
- Powder bed setup
- Printer settings and adjustments
- Printing a part, observations during printing, and instruction on changing spread and dry times
- Part removal
- Curing furnace operation (in-house curing oven)
- Curing of parts
- De-powdering of parts
- Evaluation of print quality
- Machine cleanup
- Printhead cleaning
- Fluid delivery system flushing
- Measures taken for long term machine lay-up
- Sintering and infiltration set up

In March of 2007, the modified ProMetal R2 was shipped to Montana Tech/CAMP. Ex One service personnel visited Montana Tech to install and test the titanium R2 three-dimensional printing equipment. While at Montana Tech, Ex One service personnel also removed the standard R2, which had been on loan to Montana Tech pending arrival of the titanium R2. Ex One field service personnel also trained Montana Tech personnel in the safe operation of the titanium R2. Initially, the system will

be used for printing of stainless steel powders, until Ex One engineers have completed their evaluation of suitable binders for titanium powder.

II. Baseline Unit Process Development
Alloy and Powder Characterization
Task II.1a. Acquire powder

The Ex One Company acquired several titanium and titanium alloy powders for the purpose of characterizing and sintering tests. These powders include:

- Gas Atomized Ti-6Al-4V (Crucible Compaction Metals)
- Gas Atomized TiAl (Crucible Compaction Metals)
- Gas Atomized Ti_3Al (Crucible Compaction Metals)
- CP Ti (International Titanium Powders, LLC)
- Gas Atomized Ti-6Al-4V (Carpenter Powder Products, Bridgeville, PA)
- Gas Atomized CP Ti (Carpenter Powder Products, Bridgeville, PA)

Montana Tech/CAMP acquired and characterized a gas atomized CP Ti fabricated by Advanced Specialty Metals, Inc., of Nashua, NH. Further descriptions of these powders can be found in subsequent sections of this report

Task II.1b. Chemical characterization

The following table contains analytical data for the titanium alloys represented in this report

Alloy	Al	C	Fe	H	Mo	N_2	O_2	Si	V	Ti
CP-Ti Grade II		0.1	0.3	0.015		0.03	0.25			Balance
Ti-6Al-4V	5.5 to 6.75	0.1	0.4	0.0125		0.05	0.2		3.5 to 4.5	Balance
Ti-8Al-1Mo-1V	7.35 to 8.35	0.08	0.3	0.0125	0.75 to 1.25	0.05	0.12		0.75 to 1.75	Balance
Ti-10V-2Fe-3Al	2.6 to 3.4	0.05	1.6 to 2.2	0.015		0.05	0.13		9.0 to 11.0	Balance
Ti-3.5Fe	Under Development									
Ti-1Al-8V-5Fe	Under Development									

The Certificate of Analysis provided by Capenter Powder Products with their gas atomized Ti-6Al-4V powder is as follows:

Al	C	Fe	N_2	O_2	V	Ti
6.21	0.046	0.044	0.008	0.15	3.91	Balance

The Certificate of Analysis provided by Advanced Specialty Metals with their PREP prepared Cp-Ti Grade II powder is as follows:

N_2	C	H	Fe	O_2	Si	Cl	Na	Ti
0.009	0.02	0.002	0.14	0.18	0.01	0.001	<0.0005	Balance

Task II.1c. Metallurgical characterization

The Center for Advanced Mineral and Metallurgical Processing (CAMP) has purchased a software add-on to a scanning electron microscope (SEM) located at Montana Tech. The Mineral Liberation Analyzer (MLA) technology was developed by Dr. Ying Gu of the JKTech Center of the University of Queensland.

This technology is perfectly suited for analysis and characterization of metals powders, as well as, characterizing metal alloys and phases in the final or intermediate titanium parts. For metal powders, the samples are placed into sample cups with epoxy and allowed to harden. Next, the samples are polished and carbon coated for MLA analysis.

The MLA technology utilizes back scatter scanning electron microscopic techniques along with energy dispersive x-ray analysis (EDX). Secondly, the MLA uses brightness and contrast controls on the SEM. When properly used, elements located on the periodic table will have a defined brightness number. According to theory, lower atomic number elements such as carbon, oxygen, and silicon, as well as others, will tend to be less bright when compared to heavier atomic number elements, such as copper, gold, lead, and zinc. These elements tend to be brighter when these techniques are used. This technology allows the user to do a variety of metallurgical/mineral scans.

Another advantage of the MLA technology is the ability to quantify the alloys and metallurgical aspects within the samples. During analysis, the software takes into account particle size. The software then analyzes and records the particles within the sample. At the same time, an EDX pattern is collected and saved for future elemental quantitative analysis. After collection of the received sample, the samples are microprobed using the scanning electron microscope and analytical standard measurements are taken. Samples are finally quantified metallurgically/mineralogically using the MLA software. This standard practice is done repeatedly until the unknown content is less 0.5%.

For a 1.25" diameter sample (sample cup size), the MLA software will generate several frames (images) of data. The following picture is a SEM back scatter frame (image) of the by Advanced Specialty Metals with their PREP prepared Cp-Ti Grade II powder.

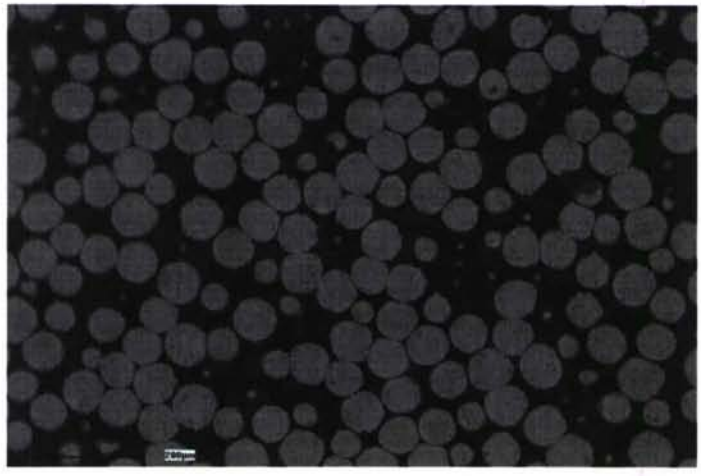

Figure 13 – SEM Back Scatter Image of CP-Ti Powder

Note that this image was taken from a polished sample, hence the 2D appearance. The next figure is from the MLA software.

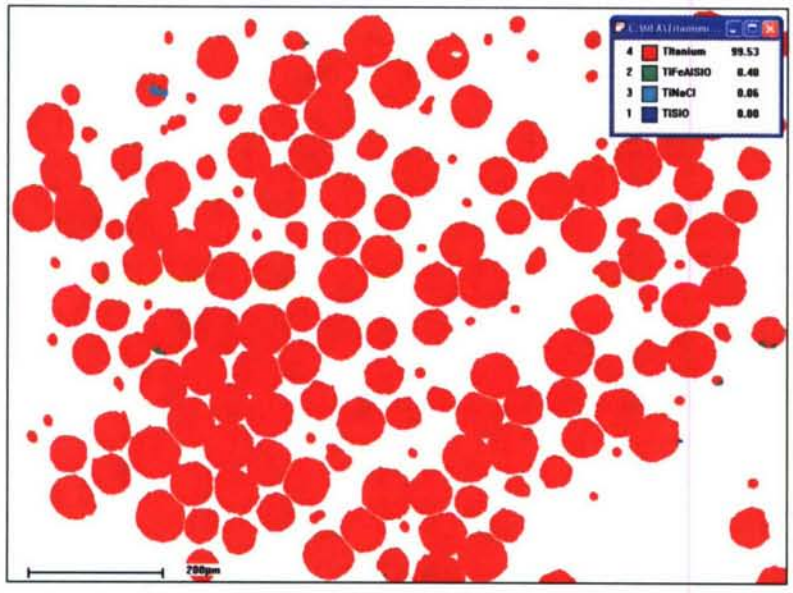

Figure 14 – MLA Image of CP-Ti Powder

The MLA software will colorize particles or phases that it deems unique. This is accomplished prior to using Energy Dispersive X-ray Analysis (EDX) capabilities of the SEM to analytically determine the content.

The following table compares the MLA software analysis with the Certificate of Analysis provided by Advanced Specialty Metals.

Method	N_2	C	H	Fe	O_2	Si	Cl	Na	Ti
C of A	0.009	0.02	0.002	0.14	0.18	0.01	0.001	<0.0005	Balance
MLA	*	*	*	0.13	0.12	0.02	0.005	0.0005	99.8

The EDX can not reliably account for elements lighter than oxygen and since the sample was coated with carbon prior to testing, it can not reliably account for carbon. With this aside, the results are reasonably comparable.

Task II.1 d. Physical characterization

One of the most crucial aspects of powder for 3DPrinting and sintering is the surface topography. This is best characterized by SEM analysis. Figure 15 shows the ITP powder after processing by the Armstrong process. The network of fibers is not suitable to shapemaking by any process, let alone 3D Printing. Figure 16 shows the material after milling. The particles are angular and fine (about 5 to 25 microns) but of sufficient roundness that they may be able to be spread by the 3DPrinter.

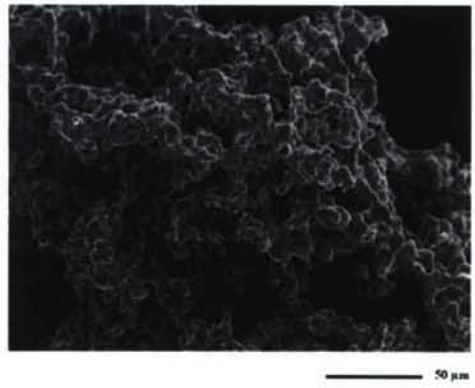

Figure 15 – Sponge Produced by ITP using the Armstrong Process

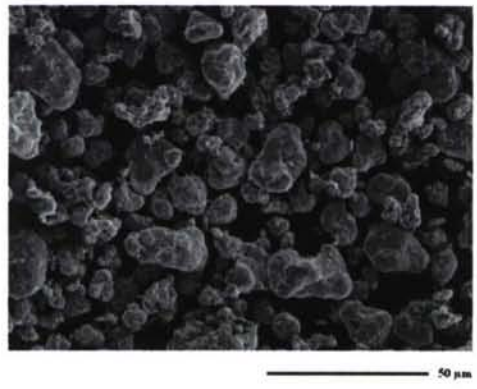

Figure 16 – ITP Powder after Milling

Figure 17 shows Ti-6Al-4V from Crucible Research. The gas atomized particles are spherical with considerable satellites attached. The particles appear to be bimodal with many of them in the 100 micron range and others below 50 microns. These powders should be spreadable.

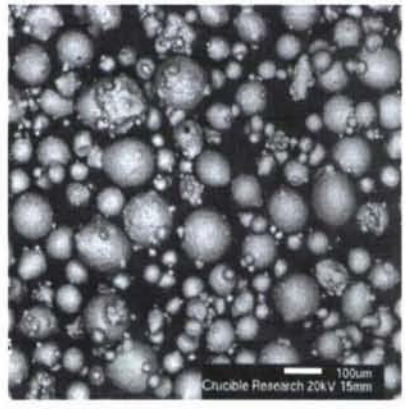

Figure 17 – Gas Atomized Ti-6Al-4V powder from Crucible Research

Figure 18 shows TiAl from Crucible Research. These gas atomized particles are highly spherical with no satellites. The particles are again bimodal, with many of them in the 50 micron range and others at 20 microns or below. Again, these powders will be spreadable.

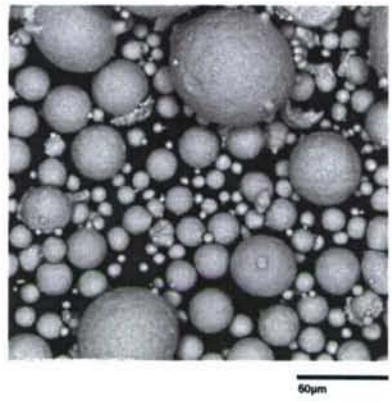

Figure 18 – Gas Atomized TiAl powder from Crucible Research

The Certificate of Analysis for PREP prepared Cp-Ti Grade II powder from Advanced Specialty Metals had the following sieve analysis (particle size) information.

Sieve	US Series	170	200	230	270	325	400	Pan
	Opening (um)	88	74	62	53	44	37	<37
% Retained on Screen		0.0	0.7	97.2	2.1	0.0	0.0	0.0
% Finer Than This Size		100.0	99.3	2.1	0.0	0.0	0.0	0.0

This test was conducted according to ASTM B214, "Standard Test Method for Sieve Analysis of Metal Powders".

Montana Tech/CAMP conducted a separate sieve analysis using ASTM E276-03 "Standard Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials" with the following results.

Sieve	US Series	170	200	230	270	325	400	Pan
	Opening (um)	88	74	62	53	44	37	<37
% Retained on Screen		0.0	0.0	50.42	49.58	0.0	0.0	0.0
% Finer Than This Size		100.0	0.0	49.58	0.0	0.0	0.0	0.0

Although, Montana Tech/CAMP found a slightly different particle size distribution, the results are comparable.

Another feature of the MLA software is the particle size analyzer. The following diagram contains the MLA generated particle size distribution.

Sample: Leo270_XBSE_spx_s.mdb
Particle Set: XBSE

Mineral Grouping: Ungrouped
Number of Particles: 6578

Size Definition: Equivalent Circle

Size Range: 4 Sqrt 2

Size	Retained (Wt%)	Cum Retained (Wt%)	Cum Passing (Wt%)
106.0		0.000	100
90.0	0.044	0.044	100
75.0	16.4	16.5	83.5
63.0	52.2	68.6	31.4
53.0	15.4	84	16
45.0	7.12	91.1	8.88
38.0	3.97	95.1	4.91
32.0	1.87	97	3.04
27.0	0.799	97.8	2.24
22.0	0.406	98.2	1.83
19.0	0.231	98.4	1.6
16.0	0.677	99.1	0.922
13.5	0.812	99.9	0.110
11.4	0.077	100	0.032
9.60	0.015	100	0.017
8.10	0.002	100	0.016
6.80	0.008	100	0.008
5.70	0.008	100	0.000
4.80		100	0.000
	P20	P50	P80
Size	55.6	67.3	74.2

Figure 19 – MLA Particle Size Analysis Table

The accompanying chart can be found below. The results from the MLA software are not comparable to the two sieve analysis. This can be attributed to the way the sample was prepared, or mainly due to the polishing. Several particles were smaller than 63 microns because of the orientation in the epoxy. By polishing these particles, you can not guarantee a perfect split on each particle. The MLA software particle size feature should be conducted on loose particles and will be done as such in the future.

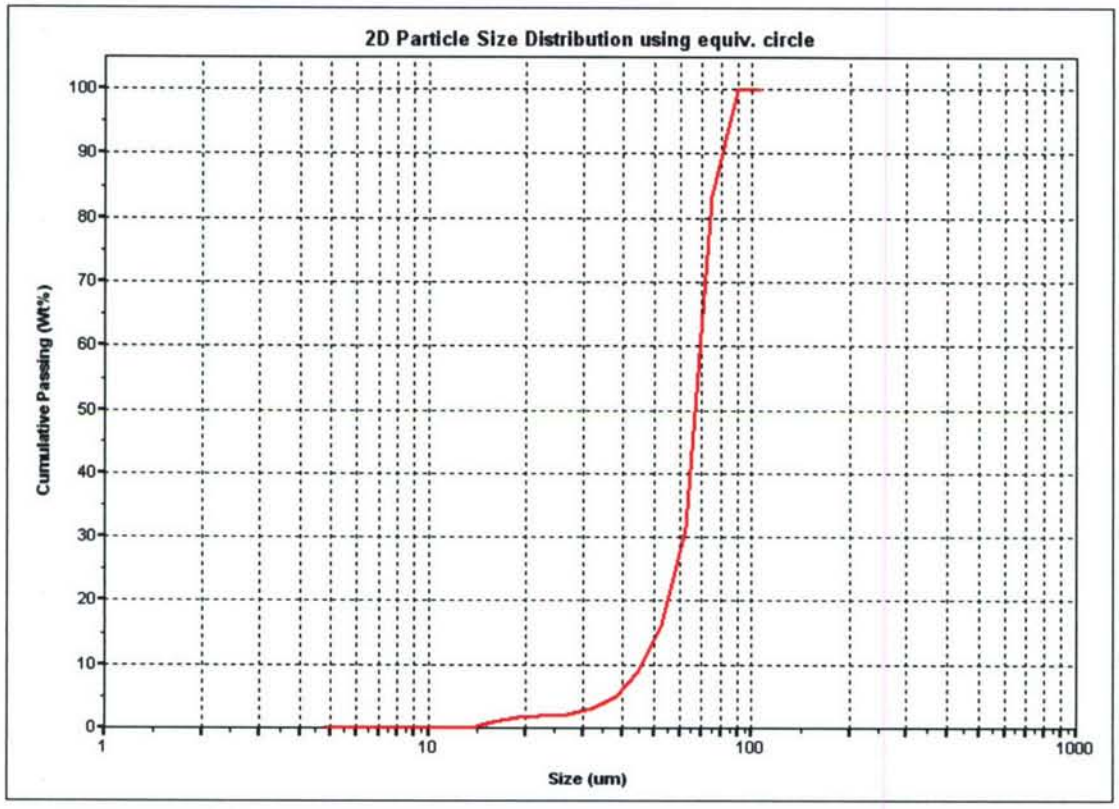

Figure 20 – MLA Particle Size Analysis Graph

Powder Spreading.

Task II.2a. Spreading tests

The ideal particle shape and size for use with the ProMetal R2 is spherical powder with an average particle size of approximately 50 microns. Through this project the Ex One Company was successful in using spherical powder with an average particle size of approximately 25 microns and irregular-shaped, jet milled powder with an average particle size of approximately 15 to 20 microns. This is considered sufficient for the powders that will be used in the second phase (year 2) of this project. It is generally believed that ultra-fine powders will create a safety risk and will be difficult to use with the ProMetal R2 air purge system that has been incorporated into the build area.

Task II.2b. Spreader alternatives

Due to the success realized in the spreading tests, alternative spreaders will not be examined.

Printing and Binder Development.

Due to a License Agreement between The Ex One Company and Montana Tech / CAMP, all binder development was conducted at the Ex One, Irwin, Pennsylvania location.

After several different binder formulations were examined, the JP05-3 1B binder, which is a new version of S-binder, with an additive of ammonium molybdate, was used for testing.

Ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_20$ is water soluble. The solubility is 43g per 100cc cold water, density 2.498g/cc, pH value 5.0 - 5.5, boiling point 190°C (decomposition), and a melting point 90°C (loses water at this temperature). During the calcination, ammonium molybdate decomposes through loss of water and ammonia, The phase formed upon calcination was expected to be molybdenum oxide (MoO_3), of about 81.0-83.0%. The molybdenum oxide can be reduced during debinding and the carbon residual from S-binder can be functioned as reductant. Therefore, the carbon residue is moved out through a reaction with molybdenum oxide.

Task II.3b. Binder formulation

See Above

Task II.3c. Binder testing for jetting

The JP05-3 1B binder tested effectively for jetting.

Task II.3d. Binder testing for printing

The ProMetal R2 parameters were adjusted for a successful print test (see thermal processing below).

Task II.3e. Binder testing for thermal processing

Initial thermal processing tests with the JP05-3 1B binder indicate that this will be the binder used for future tests.

Thermal Processing

Ti-6Al-4V

Commercial wrought alloy Ti-6Al-4V is titanium alloyed with 6% Aluminum and 4% Vanadium. This alloy has a melting point range of 1604-1660°C, which is not suitable for supersolidus liquid phase sintering. Alternatively, we propose sintering of Ti-6Al-4V via transient liquid phase sintering.

The initial test is to determine the possibility of sintering loose packing Ti alloy powder to full or near to full density. If so, Ti parts can be directly manufactured by 3DPrinting.

Traditional liquid phase sintering uses two or more small powders; upon heating, one powder melts or reacts to form a liquid between the particles. In contrast, in transient liquid phase sintering, liquid formed at the sintering temperature is soluble in the solid particles, and hence is "absorbed" during the process.

The starting materials are pure titanium powder and titanium aluminide (TiAl) powder mixture. TiAl contains 36 wt% of aluminum, therefore, 83.3 wt% of pure titanium powder and 16.7wt% TiAl powder are needed to form an alloy of Ti-6Al. Because pure titanium has a density of 4.51 g/cm3 and the theoretical density of TiAl is 3.66 g/cm3, the volume percentage of TiAl powder is 19.8 vol.%. During

sintering, approximate 20% of liquid will be more than enough to enhance densification. Vanadium can be prealloyed in titanium powder.

However, by using the mixture of pure titanium powder and titanium aluminide (TiAl) powder, the initial packing density is quite low, see Table 1. The lower initial packing density causes lower sintered density. Therefore, we add coarse Ti-6Al-4V prealloyed powder to improve the packing density. The powders were weighed on a laboratory balance and blended in a Turbula blender for 30 min. Four powder mixtures with different constitution of coarse powder were poured into a cylindrical brass container and tapped (5 strikes) to give uniform packing and weighed on a laboratory balance with accuracy of 0.01 gram for packing density measurement. The packing density is calculated from the weight of powder filling a brass container divided by the volume of the container, which has a standard volume of 25 cm3. Blended powder packs to higher densities than single modal powder.

The powders then were poured into cylindrical crucibles (1 inch inner diameter), respectively and tapped (5 strikes). Sintering was carried out in high vacuum. Sintering temperature was 1510°C, 30°C higher than the temperature of the peritectic reaction

$$L + \beta Ti \xleftrightarrow{1480^{\circ}C} TiAl$$

The sintered densities were measured by the Archimedes method.

Sintering		Shrinkage			Density Measurement		
Condition	Material	D1, mm	D2, mm	Shrinkage	Green	g/cc	Fraction
1510°C 3hrs Vac	Ti-6Al-4V #3	16.4	13.59	17.13%	0.41	3.1690	0.7170
1510°C 3hrs Vac	Ti-6Al-4V #2	16.6	14.35	13.55%	0.58	3.9776	0.8999
1510°C 3hrs Vac	Ti-6Al-4V #1	16.4	14.16	13.66%	0.54	3.7256	0.8429
1510°C 3hrs Vac	Ti-6Al-4V #0	16.6	15.15	8.73%	0.57	3.2946	0.7454

Table 1 - Ti-6Al-4V Sintering Test 1 (Loose Powder)

Where:

Fine Powder - 79.3%Ti+ 1 6.7%Tial+4V Mixed Powder
Coarse Powder - Ti-6Al-4V prealloyed powder (crucible research. 100- powder 325 mesh)

- **Ti-6-4 #3** - 0% coarse
- **Ti-6-4 #2** 50% coarse
- **Ti-6-4 #1** 70% coarse
- **Ti-6-4 #0** 100% coarse

The powder blended with 50% of coarse powder packs to higher density. The second test powder mixture Ti-6-4 #2 was used to test the binder and sintering temperature. The binder was mixed with Ti-6-4 #2 powder and formed in cylindrical crucibles, Figure 21.

	Dimension				Density	
Sintering Condition	D1, mm	D2, mm	D3, mm	h, mm	g/cc	Fraction
Green	14.84	14.88	14.90	16.00	2.6230	0.5934
1475°C 3hrs Vac	13.42	13.47	13.34	14.59	3.6510	0.8260
1485°C 3hrs Vac	13.25	13.37	13.40	14.48	3.7303	0.8440
1495°C 3hrs Vac	12.99	13.08	13.21	14.56	3.8229	0.8649
1505°C 3hrs Vac	13.01	12.95	13.17	14.14	3.7646	0.8517
1510°C 3hrs Vac	12.82	12.73	12.88	13.97	3.8981	0.8819

Table 2 - Ti-6Al-4V Sintering Test 1 (50% Coarse Powder with Binder)

Where:

Binder – RM-DB017-6-4 Gold Binder Trial Formula
Debinding - 5°C/min to 200°C for 30 minutes, 2°C/min to 400°C for 30 minutes, and 5°C/min to 500°C for 30 minutes.
Atmosphere – 100% Argon Gas

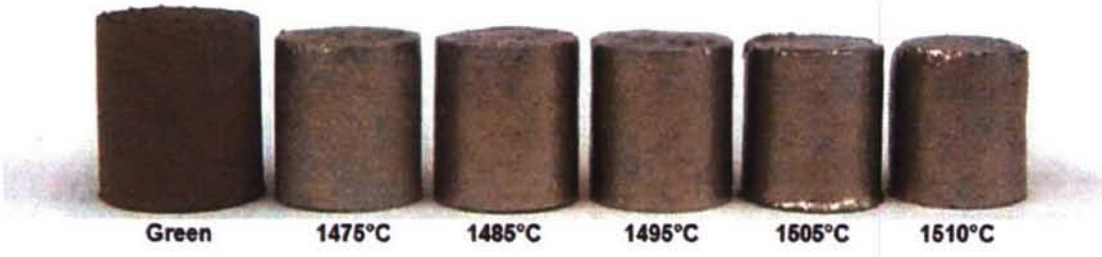

Figure 21 – Sintered Compacts of Ti-6Al-4V

Microstructural analysis shows the sample with 50% coarse powder sintered at 15 10°C contained heavy amounts of pores in the center (20+%) and lighter amounts along the edge (5+%). Figure 22 is a macro picture of this sample to illustrate the heavy to light porosity areas. The lighter area located in the center of the sample contains the heavy porosity and the darker area actually represents the areas of lighter porosity. The sample did not appear to have any segregation. Figure 23 on the edge and Figure 24 is the microstructure in the center.

Though the sample has low overall density, the pores on the edge are all closed. This result indicates that the sintered parts can be directly hot isostatically pressed without encapsulation.

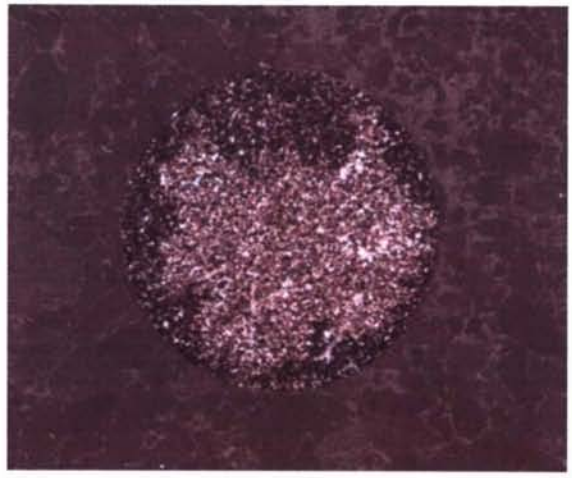

Figure 22 – Macrograph Showing High Porosity in the Center

Figure 23 – Macrograph Showing Closed Pore Porosity

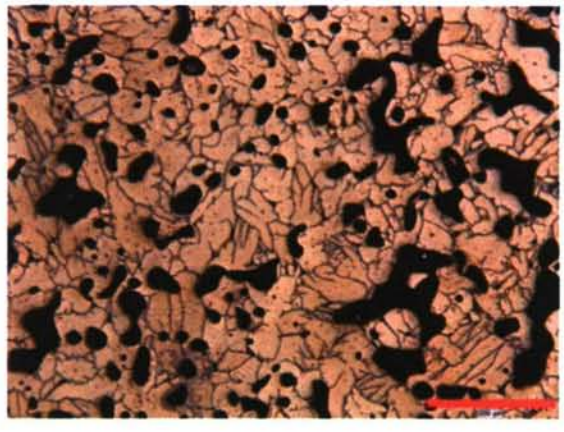

Figure 24 – Macrograph Showing High Porosity in the Center

Ti-8Al-1Mo-1V

Sintering trials were performed at the Ex One Company of Irwin, Pennsylvania, on the near-alpha alloy Ti-8Al-1Mo-1V. The three base alloys plus elemental Mo were mixed in the proper proportions to achieve the desired composition. Ceramic crucibles of the powder mixtures were sintered under various furnace profiles in vacuum to determine the optimum sintering conditions. The sintered materials are shown in Figure 25.

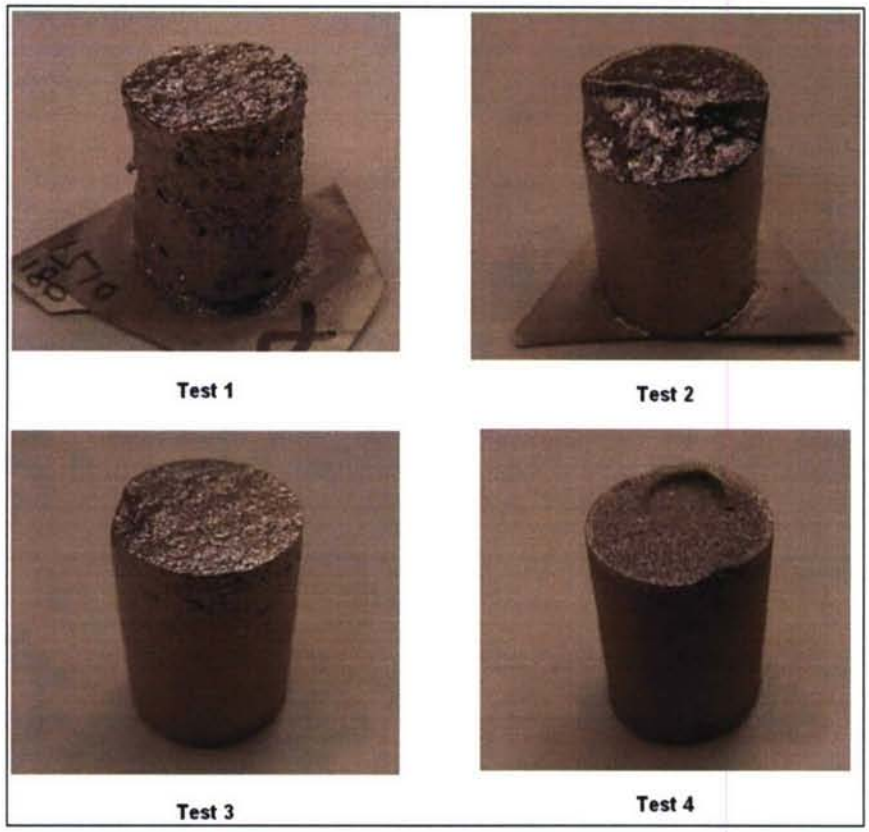

Figure 25 – Sintered Compacts of Ti-8Al-1Mo-1V

- Test 1 - 5°C/min to 1510°C for 180 min, 5°C/min cool down
- Test 2 - 5°C/min to 1490°C for 180 min, 5°C/min cool down
- Test 3 - 5°C/min to 1280°C for 30 min, 2°C/min to 1480°C for 180 min, 2°C/min to 1430°C for 60 min, 5°C/min cool down
- Test 4 - 5°C/min to 1470°C for 180 min, 5°C/min cool down

To determine the porosity levels, the sintered compacts were weighed, and then reweighed after impregnation with liquid wax. The impregnated samples were also weighed in water. This provided the density of the compact with all porosity included, and the amount of open porosity (porosity on the surface). The calculation formulae are given below:

W1 = weight of the sample

W2 = weight after impregnation with liquid wax
W3 = weight of impregnated sample in water.
Density = W1/(W2-W3),
Fractional Density = Density/Theoretical Density
Theoretical Density = 4.37 g/cc
Open porosity = (W2-W1) /(W2-W3) x 100%
Total porosity = (1 - Fractional Density) x 100%

Temp °C	W1	W2	W3	Density	Fractional Density	Open Porosity	Total Porosity
1470	6.9155	7.0402	5.0769	3.5224	0.8060	6.35%	19.40%
1480	6.8325	6.8710	4.9599	3.5752	0.8181	2.01%	18.19%
1485	7.3638	7.3870	5.1462	3.2862	0.7520	1.04%	24.80%
1490	6.9841	6.9893	4.9221	3.3785	0.7731	0.25%	22.69%

Table 3 - Sintering temperatures, weights and densities for the four sintered compacts in Figure 3

Table 3 gives the results. Although the porosity levels actually increase with increasing temperature, the amount of open porosity decreases substantially. For sintering temperatures above 1485 C, the open porosity is below 1%. This implies that the surface porosity is closed and the parts could be HIPed to full density without using a mold. The micrographs below, illustrate the distribution of porosity, which was measured by digital analysis. Clearly the porosity is very high and does not lead to a useable material. Further sintering tests will be performed in an effort to determine parameters that will lead to high density and useable material.

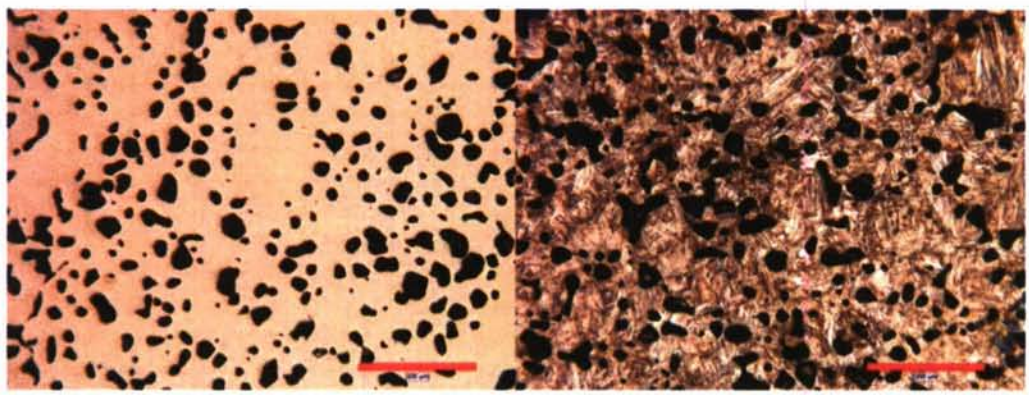

Figure 26 - Sintered @ 1470°C for 180 Minutes, Porosity @ Edge = 14.7% Porosity @ Center = 25.9%

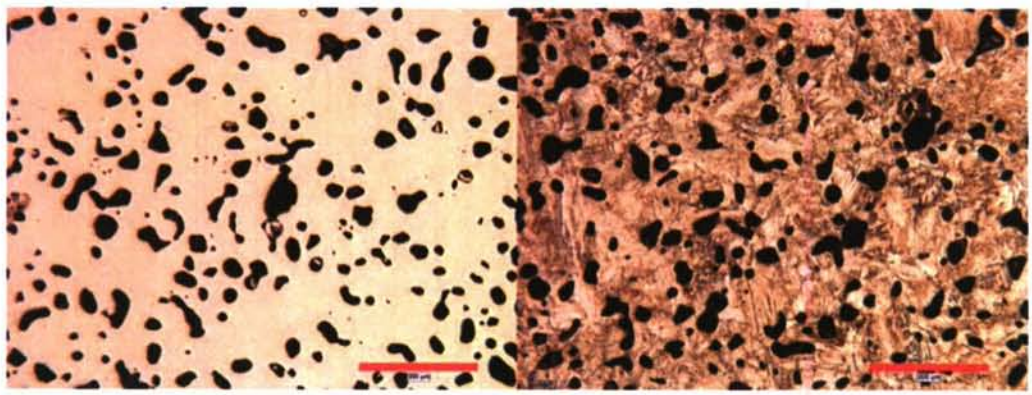

Figure 27 - Sintered @ 1480°C for 180 Minutes, Porosity = 17.3%

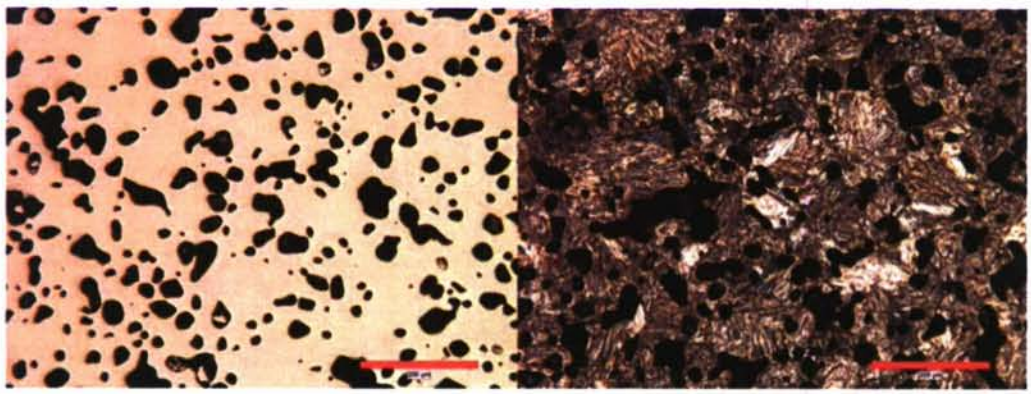

Figure 28 - Sintered @ 1485°C for 180 Minutes, Porosity = 25.9%

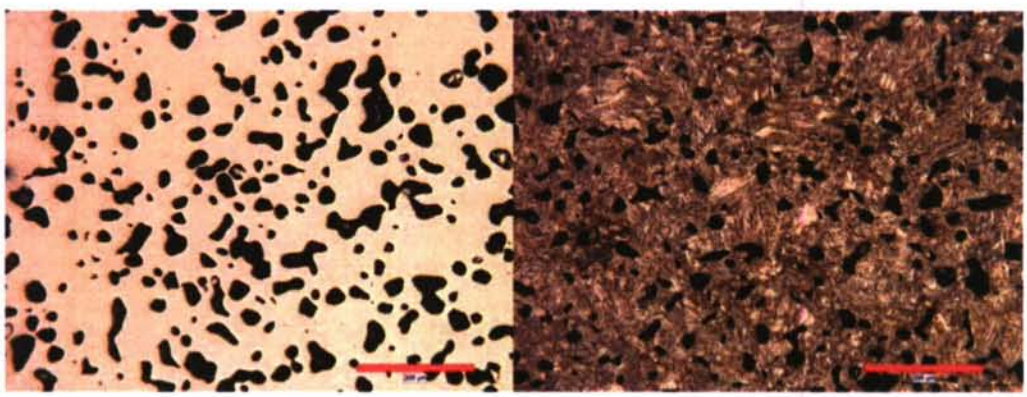

Figure 29 - Sintered @ 1490°C for 180 Minutes, Porosity @ Edge = 18.7%
Porosity @ Center = 24.9%

Ti-10V-2Fe-3Al (In Vacuum)

In addition, sintering tests were performed on the metastable beta alloy Ti-10V-2Fe-3Al. Metastable beta alloys are characterized by high hardenability, with the metastable beta phase completely retained on air cooling of thin sections or on water quenching of thick sections. The beta phase is usually metastable and has a tendency to transform to the equilibrium alpha plus beta structure. After solution treatment, metastable beta alloys are aged at temperatures of 450°C to 650°C (850°F to 1200°F) to partially transform the beta phase to alpha. The alpha forms as finely dispersed particles in the retained beta, and strength levels comparable or superior to those of aged alpha-beta alloys can be attained. The chief disadvantages of beta alloys in comparison to alpha-beta alloys are higher density, lower creep strength, and lower tensile ductility in the aged condition. Although tensile ductility is lower, the fracture toughness of an aged beta alloy generally is higher than that of an aged alpha-beta alloy of comparable yield strength. Very high yield strengths (about 170 ksi) with excellent toughness ($K_{IC} \approx$ 40 ksi $\sqrt{in}$) have been claimed for the beta alloy Ti-10V-2Fe-3Al.

Sintering tests were performed on the metastable beta alloy under seven different sintering conditions. Metallography was performed on two of the samples and the micrographs are shown in Figure 2 below. In this case the porosity levels are lower than for the near-alpha alloy above, but they are still unacceptable, and further sintering tests will be performed.

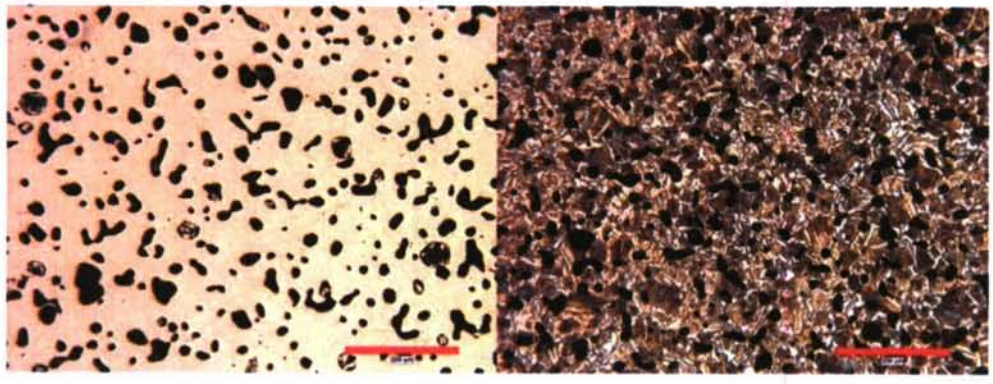

Figure 30 - Sintered @ 1100°C for 30 minutes, 1430°C for 30 minutes, and 1432°C for 180 minutes, Porosity = 14.3%

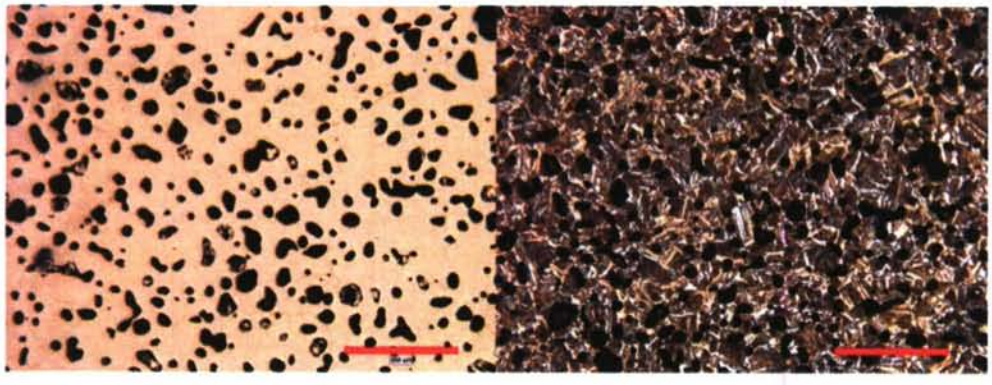

Figure 31 - Sintered @ 1280°C for 30 minutes, 1428°C for 10 minutes, and 1430°C for 180 minutes, Porosity = 15.8%

While conventional compaction processes are used to produce titanium powder metal parts, the perform density is greater than 80% and sintering to near full density, although difficult, is feasible. In the present case the starting density of the printed powders is near 50%. Sintering to full density from such a low density is problematic, as shown in the above micrographs. Because of its high reactivity, titanium readily sinters initially at the junction points. However, densification to near full density by sintering mechanisms alone is made difficult by this same reactivity. Adsorbed gases and impurities impede sintering to full density. Generally, mechanical loads, such as hydrostatic pressure (HIPping) or powder forging are necessary to achieve full density. For this reason, our future efforts will focus on reaching low levels of surface and open porosity so that HIPping can be used to reach full density.

Processing Gas Atomized Ti-6Al-4V Spherical Powder

The first test was carried out on gas atomized Ti-6Al-4V spherical powder (-270 mesh +22μm). The powder was provided by Carpenter Powder Products, Bridgeville, PA.

Ti	Al	V	Fe	C	O	N
Balance	6.21	3.91	0.044	0.046	0.15	0.008

Table 4 - Chemical analysis (by Carpenter)

Six cylindrical specimens were printed and half of the specimens were cured in air, which is the standard curing method, the other half were cured in a CM furnace under argon atmosphere. After being cured, both were debound in the CM furnace under an atmosphere of 70% argon and 30% hydrogen.

Thermal characteristics of debinding

- 5°C/min to 230°C for 30 min
- 5°C/min to 330°C for 30 min
- 5°C/min to 550°C for 60 min
- (unfortunately all the specimens lost green strength)

Carbon and oxygen contents were measured in the original powder, the specimens after curing and specimens after debinding.

Sample	Carbon content, wt%			Average
Ti-6Al-4V powder	0.05 873	0.06608	0.06682	0.063 88
Cured in air	0.7722	0.7650	0.7286	0.7553
cured in Ar	0.7797	0.8762	0.75 12	0.8024
Cured in air then debinded at 550°C in H2	0.1494	0.1392	0.1465	0.1450
Cured in Ar then debinded at 550°C in H2	0.1473	0.1555	0.1434	0.1487

Table 5 - Carbon content

Sample	Oxygen content, wt%			Average
Ti-6Al-4V powder	0.13 87	0.1669	0.1572	0.1543
Cured in air	0.5652	0.5631	0.5821	0.5701
cured in Ar	0.6532	0.6518	0.7347	0.6799
Cured in air then debinded at 550°C in H2	0.1561	0.2678	0.2429	0.2223
Cured in Ar then debinded at 550°C in H2	0.2085	0.2027	0.2075	0.2062

Table 6 - Oxygen content

One evaluation of hydrogen content of the debound sample showed the specimen may contain up to 2.3% hydrogen, compared 200ppm in normal titanium alloy. This result indicated that during debinding, the green specimens absorbed a significant amount of hydrogen and stored it in the materials.

The debound specimens were sintered at 1360°C for 180 min in the Centorr furnace under vacuum. During heating, the vacuum level went down to 10^{-4} at a temperature range between 600-800°C, and then to 10^{-6} when the temperature increased. It is supposed that hydrogen was released as a result of the thermal decomposition of titanium hydrides in a vacuum.
After sintering in a vacuum atmosphere, hydrogen, oxygen, and carbon were measured. The data shows that debinding in hydrogen, followed by sintering in a vacuum atmosphere, dramatically decreases oxygen in the final sintered specimen. Oxygen level is reduced from 0.15% of original powder to 0.06% after sintering. Hydrogen was found to be below 200ppm.

Element	Data			Average
H_2, ppm	157.0	205.0	104.0	155.3
O_2, wt%	0.06406	0.05744	0.06129	0.06093
C, wt%	0.1623	0.1774	0.1542	0.1646

Table 7 - Chemical analysis after sintering

As a result of the tests above, some conclusions were achieved:

1. The printed titanium powder cured in air does not gain extra oxygen.
2. The cured parts debound in hydrogen absorb hydrogen, however, the absorbed hydrogen is removed in the subsequent sintering under vacuum.
3. Debinding in hydrogen followed by sintering in a vacuum is similar to a hydride-dehydride process, which dramatically reduces the oxygen in the final sintered specimen.

Hydride-dehydride is a reversible process. In the current research, this process was used to aid debinding and reduce the oxygen level in the sintered specimen. We expect that this debinding-sintering technology will help reduce oxygen levels of low cost titanium powder.

The hydride-dehydride process, in particular, is commonly employed in the manufacture of low-cost and low oxygen titanium powder. In the hydride-dehydride process, metallic pieces are embrittled by gaseous hydrogen, yielding the corresponding hydrides. These brittle hydrides are milled, sieved, and dehydrated in vacuum at high temperatures to obtain the corresponding metallic powders.

Another five specimens were printed, cured in air, three debound with profile 1 and another two debound in profile 2, and then sintered under vacuum. The difference between profiles 1 and 2 is the former were cooled in argon and the latter cooled in a mixture of argon and hydrogen.

Profile 1	Profile 2
5°C/min to 230°C for 30 min in 112	5°C/min to 230°C for 30 min in 112
5°C/min to 330°C for 30 min in 112	5°C/min to 330°C for 30 min in 112
5°C/min to 550°C for 60 min in 112	5°C/min to 550°C for 60 min in 112
Cool in Ar	Cool in H_2/Ar

Sintering was carried out at temperatures from 1400°C to 1360°C for 180 min. The sintered densities were measured by the Archimedes method.

Figure 32 - Sintered specimens - the three on left were debound with Profile 1 and the two on right were debound with Profile 2. All specimens were sintered in vacuum.

Temp. °C	W1, g	W2, g	W3, g	density, g/cc	fraction
1440	4.0011	4.1391	3.0457	3.6593	0.8121
1420	4.0116	4.1643	3.0532	3.6105	0.8013
1400	4.0460	4.1993	3.0750	3.5987	0.7986

Table 8- Sintered density of printed gas atomized Ti-6Al-4V spherical powder

Sintering fine powder is relatively easy, but processing fine spherical titanium powder does increase the combustion risk of processing, because titanium is very reactive. Additionally, the cost of three-dimensionally printed parts utilizing this powder is higher, because of the high cost for manufacturing such powder. Furthermore, the green specimens lost their green strength after debinding making them difficult to handle after debinding.

Sintering Gas Atomized CP Ti Spherical Powder With Mixed Iron

Below is the phase diagram of titanium and iron. It shows that at 1085°C Ti and Fe forms eutectic liquid and, when the temperature increases to 1289°C, another iron rich liquid phase forms. When sintering is carried out above 1300°C, the mixed powder forms iron rich liquid first on the surface of titanium particles. After iron diffuses into the titanium particles, a second liquid phase forms. Further diffusion reduces the liquid phase and eventually the liquid disappears and forms a single β-phase titanium alloy. This is a two-stage transition liquid phase sintering process. There is no intermetallic compound formed when temperature is above 1427°C. Obviously, iron is the element enhancing densification in sintering.

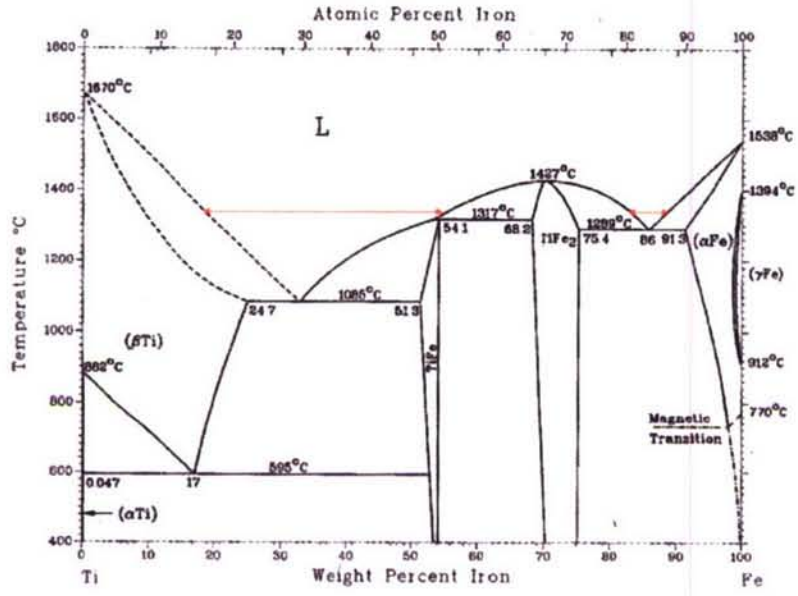

Figure 33 - Ti-Fe binary phase diagram

The current binder works very well for iron based alloys. Therefore, if the titanium powder is mixed or coated with iron (a coating process is preferred so that the iron covers all surface of titanium particles and forms metallurgical bond between iron and titanium), the whole process, which includes printing, debinding, and handling, will be much safer and easier. For example, green parts can be presintered up to 1000°C immediately after debinding for handling strength.

The second sintering test used gas atomized CP Ti spherical powder with a larger particle size (-100+325mesh) mixed with 2% and 4% carbonyl iron powder, respectively. The powders then were poured into cylindrical crucibles. Sintering was carried out at temperatures from 1200°C to 1440°C for 180 minutes under vacuum. The sintered densities were measured by the Archimedes method.

Samples	W1, g	W2, g	W3, g	Density, g/cc	Fraction
1440-2	12.3310	12.5730	9.4822	3.9896	0.8854
1440-4	13.5506	13.7095	10.4886	4.2071	0.9337
1420-2	13.3945	13.7775	10.2942	3.8453	0.8534
1420-4	14.1324	14.4627	10.9097	3.9776	0.8827
1400-2	12.5088	12.8783	9.6152	3.8334	0.8507
1400-4	10.5802	10.8144	8.1810	4.0177	0.8916
1380-2	13.3496	13.7968	10.2504	3.7643	0.8354
1380-4	14.9974	15.3647	11.5830	3.9658	0.8801
1360-2	15.1653	15.6854	11.6378	3.7467	0.8315
1360-4	16.0847	16.4291	12.4191	4.0111	0.8902
1340-2	15.3155	15.8577	11.7425	3.7217	0.8259
1340-4	12.6133	12.9340	9.7314	3.9385	0.8740
1320-2	12.4120	12.8954	9.5119	3.6684	0.8141
1320-4	12.9612	13.2981	9.9998	3.9297	0.8721
1300-2	17.4576	18.1165	13.3879	3.6919	0.8193

Samples	W1, g	W2, g	W3, g	Density, g/cc	Fraction
1300-4	15.7803	16.2265	12.1670	3.8873	0.8627
1200-2	17.3402	18.3952	13.2142	3.3469	0.7428
1200-4	15.6711	16.4601	12.0189	3.5286	0.7831

Table 9- Sintered density of gas atomized CP Ti spherical powder with mixed iron

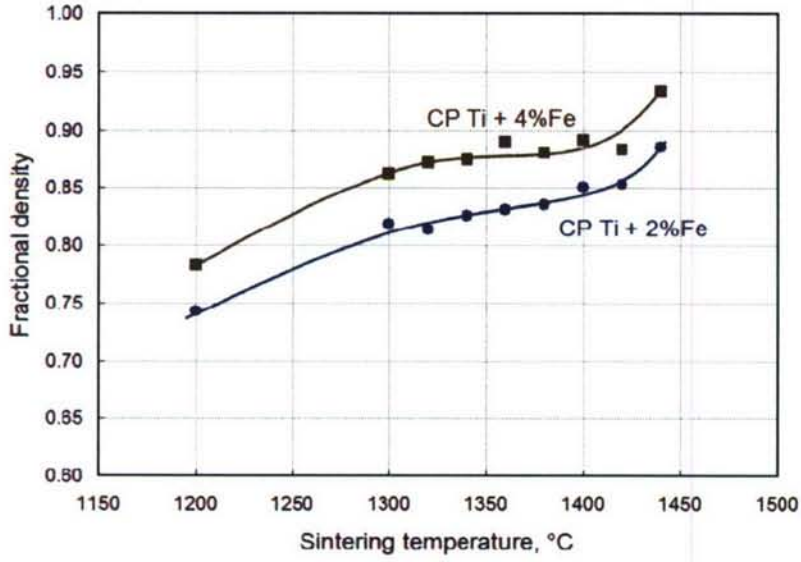

Figure 34- Density vs. Sintering Temperature

Sintering a pure metal powder with a large particle size in solid state to a density close to theoretical density is very difficult if not impossible. The above test shows that with a small fraction of iron mixed with the CP Ti spherical powder (particle size
-100+325mesh) a density over 93% of full density is achievable. Please note that the iron should not be prealloyed, the iron has to stay on the surface of the titanium particles to be effective in forming a transient liquid phase.

The β-titanium alloys which include iron as alloying element are Ti-3.5Fe, Ti-10V-2Fe-3Al, and Ti-1Al-8V-5Fe.

Sintering ITP Low Cost Titanium Powder

The Armstrong process, developed by International Titanium Powder (ITP), Lockport, IL, is a modification of the Hunter Method. In the Hunter process titanium tetrachloride (TiCl4) is reacted with sodium (Na) in a reactor vessel to produce a titanium sponge and NaCl in batch mode. In the Armstrong process titanium powder is made continuously as shown in the schematic drawing, rather than a batch method.

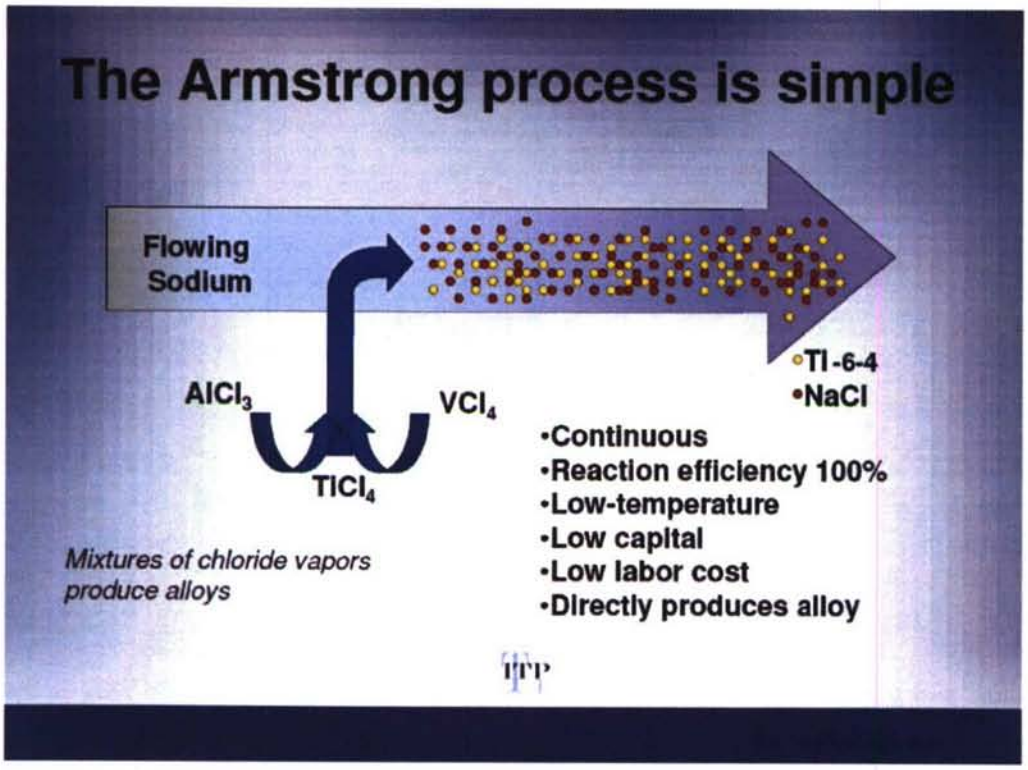

Figure 35 - Armstrong process

The Armstrong standard product is free flowing with an apparent density in a range of 0. 3g/cc to 0.5 g/cc. The powder used here has been jet milled, and has an apparent density of 1.13 g/cc and tap density of 1.49 g/cc.

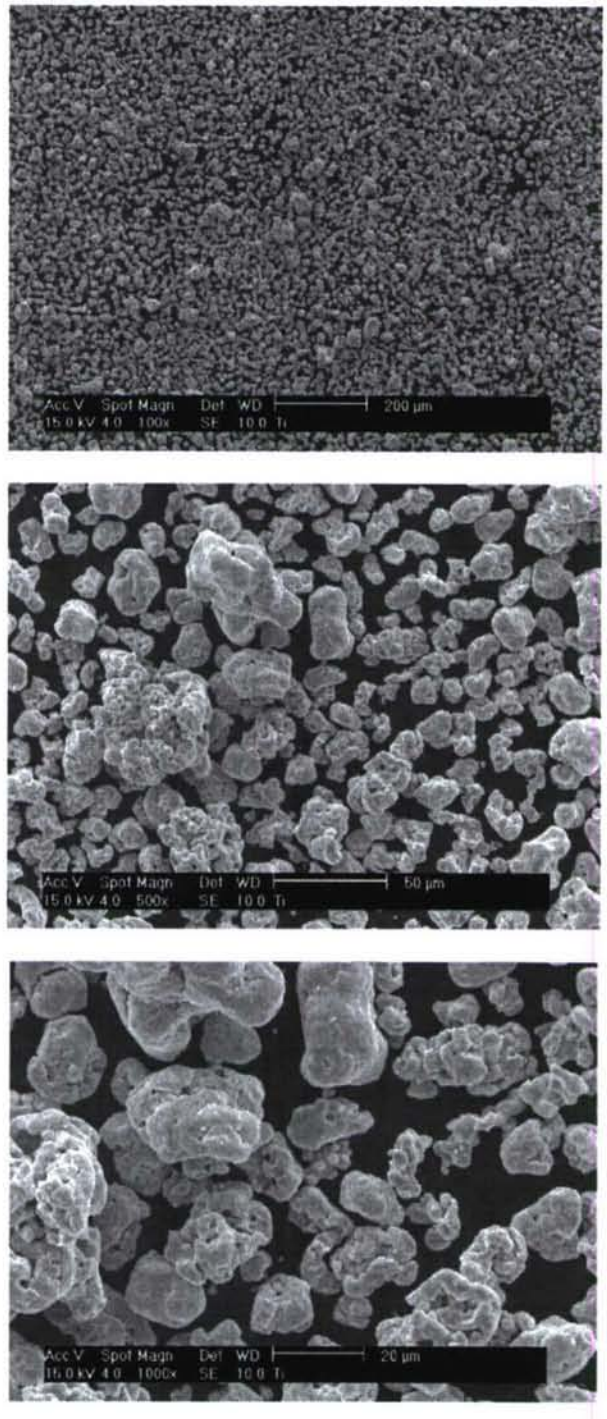

Figure 36 - SEM pictures of titanium powder as received.

Printing

Low cost titanium powder of R15U2 mixed with 3.5wt% carbonyl iron powder (CIP) was printed with JP05-31B binder into 15 mm diameter and 10 mm high cylinders and cured in air. The printed density is 33% of full density, which is similar to the tap density of the powder.

Debinding and presintering

4/17/2007

- 5°C/min to 230°C for 30 min Ar (40 SCFH) + H2 (25 SCFH)
- 5°C/min to 330°C for 30 min Ar (40 SCFH) + H2 (25 SCFH)
- 5°C/min to 550°C for 60 min Ar (40 SCFH) + H2 (25 SCFH)
- 5°C/min to 900°C for 60 min Ar (50 SCFH)

Where SCFH stands standard cubic feet per hour.

The parts had exceptionally good strength after debinding and presintering. Cracks were found at the bottom of the parts due to friction between the parts and the alumina plates the parts rested on during sintering.

4/18/2007

- 5°C/min to 230°C for 30 min Ar (40 SCFH) + H2 (25 SCFH)
- 5°C/min to 330°C for 30 min Ar (40 SCFH) + H2 (25 SCFH)
- 5°C/min to 550°C for 60 min Ar (40 SCFH) + H2 (25 SCFH)
- 5°C/min to 800°C for 60 min Ar (50 SCFH)

Similar cracks were found on the bottom of the parts.

4/20/2007

5°C/min to 230°C for 30 min Ar (45 SCFH) + H2 (5 SCFH) 5°C/min to 330°C for 30 min Ar (45 SCFH) + H2 (5 SCFH) 5°C/min to 550°C for 60 min Ar (45 SCFH) + H2 (5 SCFH) 5°C/min to 850°C for 30 min Ar (50 SCFH)

Parts were debinded on a molybdenum plate. Parts stuck slightly on the plates and were cracked

4/23/2007

- 5°C/min to 230°C for 30 min Ar (45 SCFH) + H2 (5 SCFH)
- 5°C/min to 330°C for 30 min Ar (45 SCFH) + H2 (5 SCFH)
- 5°C/min to 550°C for 60 min Ar (45 SCFH) + H2 (5 SCFH)
- 5°C/min to 850°C for 30 min Ar (50 SCFH)

Parts were debound in a zirconia crucible. No cracks were found.

Sintering test

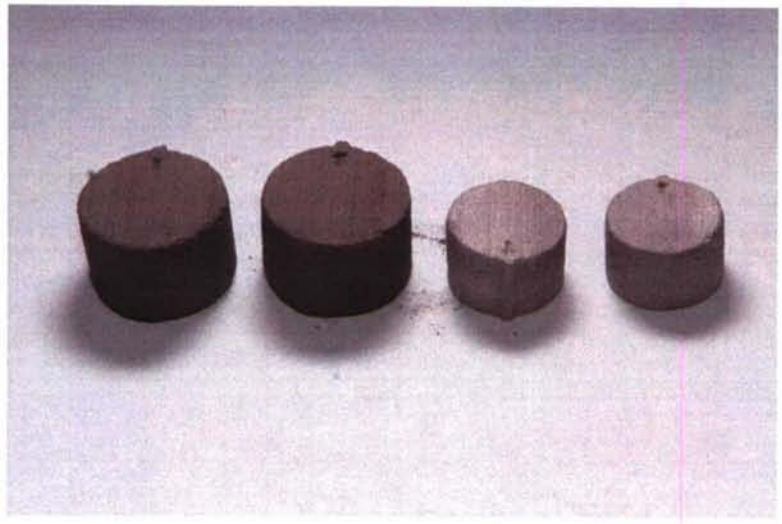

Figure 37 - Pre- and post-sinter parts

Sintering profile 14-2

- 5°C/min to 400°C Vacuum
- 2°C/min to 850°C Vacuum
- 5°C/min to 1440°C for 180 min Vacuum

Samples	Density, g/cc	Fraction
Ti+3.5%Fe	3.4797	0.7722

Microstructure

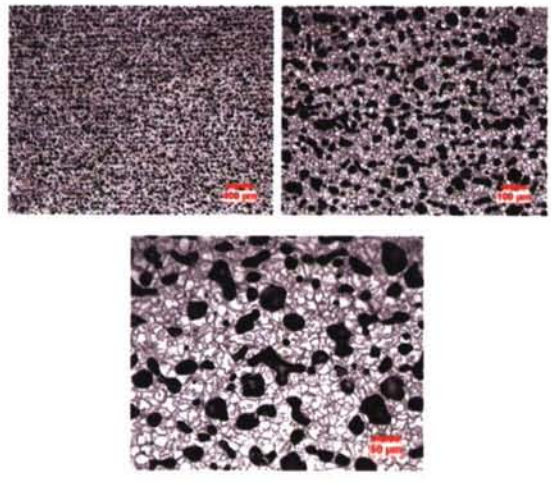

Figure 38 - Microstructure after sintering

The pores inside the particles are difficult to eliminate during sintering. The sintered densities are not more than 80% of full density. The schematic microstructure of the original powder and the sintered microstructure are shown in the Figure below.

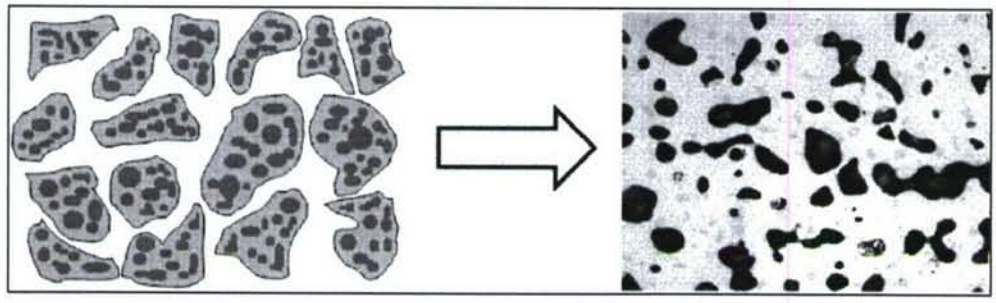

Figure 39. Schematic of microstructure before and after sintering

Sintering Gas Atomized Ti-6Al-4V Spherical Powder + 3.5% CIP Printing

Obviously, higher initial densities are desirable to achieve high sintered densities. In this test gas atomized Ti-6Al-4V spherical powder (-270 mesh +22μm) was mixed with 3.5wt% carbonyl iron powder (CIP) and was printed with JP05-31B binder. Parts were 15 mm diameter and 10 mm high cylinders that were cured in air. The printed density was 50% of full density.

Debinding and presintering

- 5°C/min to 230°C for 30 min Ar (45 SCFH) + H2 (5 SCFH)
- 5°C/min to 330°C for 30 min Ar (45 SCFH) + H2 (5 SCFH)
- 5°C/min to 550°C for 60 min Ar (45 SCFH) + H2 (5 SCFH)
- 5°C/min to 850°C for 30 min Ar (50 SCFH)

Sintering

Profile 14-3

- 5°C/min to 400°C Vacuum
- 2°C/min to 1070°C Vacuum
- 5°C/min to 1440°C for 180 min Vacuum

Samples	Density, g/cc	Fraction
Ti+3.5%Fe	3.4432	0.7641
Ti-6-4 +3.5%Fe	4.0162	0.89 13
Ti-6-4 +3.5%Fe	3.865 1	0.8578

Profile 14-4

- 5°C/min to 400°C Vacuum
- 2°C/min to 1070°C for 60 min Vacuum
- 5°C/min to 1440°C for 360 min Vacuum

Samples	Density, g/cc	Fraction
Ti-6-4 +3.5%Fe	4.1348	0.9176
Ti-6-4 +3.5%Fe	4.1330	0.9172

Profile 14-5

- 5°C/min to 400°C Vacuum
- 2°C/min to 1280°C for 180 min Vacuum
- 5°C/min to 1440°C for 60 min Vacuum

Samples	Density, g/cc	Fraction
Ti+3.5%Fe	3.2052	0.7113
Ti-6-4 +3.5%Fe	3.8532	0.855 1
Ti-6-4 +3.5%Fe	3.8293	0.8498

Profile 14-6

- 5°C/min to 400°C Vacuum
- 2°C/min to 1280°C for 180 min Vacuum
- 5°C/min to 1440°C for 180 min Vacuum

Samples	Density, g/cc	Fraction
Ti+3.5%Fe	3.5148	0.7800
Ti-6-4 +3.5%Fe	4.0272	0.8937
Ti-6-4 +3.5%Fe	3.9241	0.8709

Profile 14-7

- 5°C/min to 400°C Vacuum
- 2°C/min to 1280°C for 60 min Vacuum
- 5°C/min to 1440°C for 360 min Vacuum

Samples	Density, g/cc	Fraction
Ti+3.5%Fe	3.5304	0.7835
Ti-6-4 +3.5%Fe	4.1220	0.9148
Ti-6-4 +3.5%Fe	4.1278	0.9161

Profile 14-8

- 5°C/min to 1280°C for 60 min Vacuum
- 5°C/min to 1440°C for 120 min Vacuum
- 5°C/min to 1450°C for 60 min Vacuum

Samples	Density, g/cc	Fraction
Ti-6-4 +3.5%Fe	4.0306	0.8945
Ti-6-4 +3.5%Fe	4.0061	0.8891

Profile 14-9

- 5°C/min to 1280°C for 60 min Vacuum
- 5°C/min to 1440°C for 360 min Vacuum
- 5°C/min to 1445°C for 360 min Vacuum

Samples	Density, g/cc	Fraction
Ti-6-4 +3.5%Fe	4.2546	0.9442

Ti-6-4 +3.5%Fe	4.2534	0.9439

All the following samples are Ti-6-4 +3.5%Fe)

Profile 14-10

- 5°C/min to 1280°C for 60 min Vacuum
- 5°C/min to 1440°C for 480 min Vacuum
- 5°C/min to 1445°C for 480 min Vacuum

Samples	Density, g/cc	Fraction
1	4.2771	0.9492
2	4.2870	0.9514
3	4.3127	0.9571

Microstructure of sample # 3 profile 14-10, Ti-6-4 + 3.5%Fe. Etched microstructure typical acicular grain structure of α-Titanium.

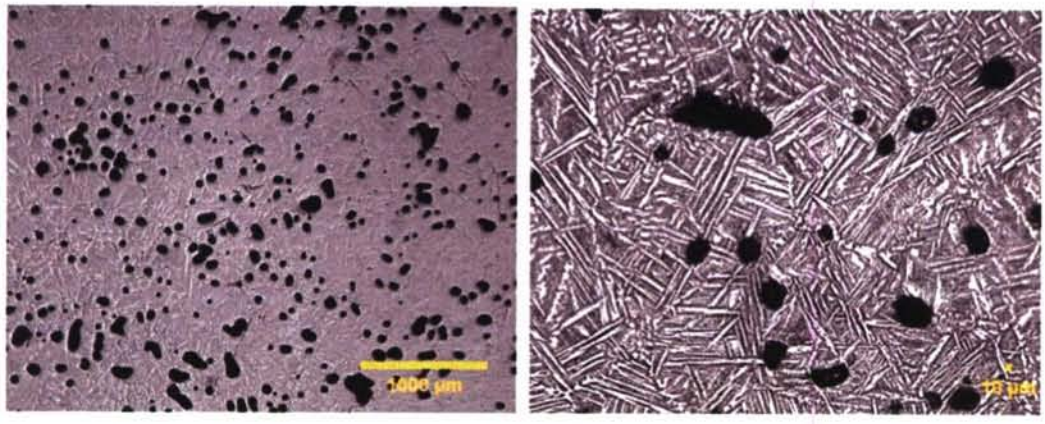

Figure 40 - Microstructure of sample # 3

Profile 14-11

- 5°C/min to 1280°C for 360 min Vacuum
- 5°C/min to 1440°C for 360 min Vacuum
- 5°C/min to 1445°C for 360 min Vacuum

Samples	Density, g/cc	Fraction
1	4.2574	0.9448
2	4.2644	0.9464
3	4.2577	0.9449

Profile 14-12

- 5°C/min to 1280°C for 360 min Vacuum
- 5°C/min to 1440°C for 360 min Vacuum
- 5°C/min to 1450°C for 360 min Vacuum

Samples	Density, g/cc	Fraction
1	4.2655	0.9466
2	4.2786	0.9495
3	4.2952	0.9532
4	4.2432	0.9417

Profile 14-13

- 5°C/min to 1280°C for 360 min Vacuum
- 5°C/min to 1440°C for 480 min Vacuum
- 5°C/min to 1450°C for 480 min Vacuum

Samples	Density, g/cc	Fraction
1	4.2755	0.9488
2	4.3066	0.9558
3	4.2336	0.9395

Task 11.4a. Sintering furnace profile determination

From the work completed by the Ex One Company of Irwin, Pennsylvania, the following graph depicts the optimized debinding and pre-sintering profile conducted in a sintering furnace with the indicated inert gas flow.

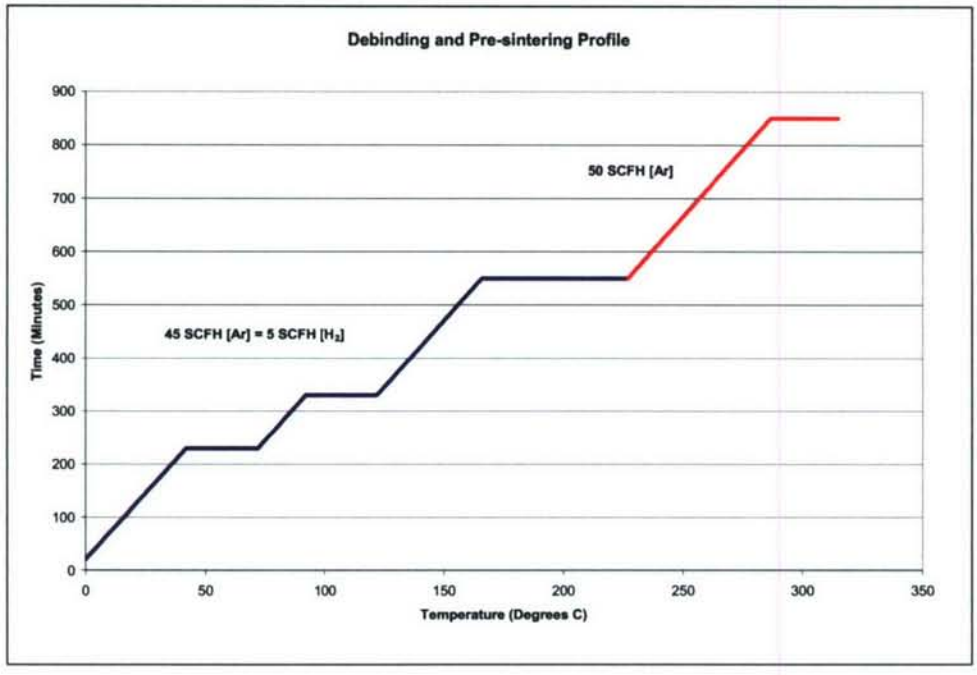

Figure 41 – Debinding and Pre-sintering Profile

Ex One completed several sintering tests and the following diagram contains the sintering profile for Ti-6-4 + 3.5%Fe which resulted in a 95.71% dense structure. The sintering cycle was preformed in a sintering furnace with a vacuum atmosphere.

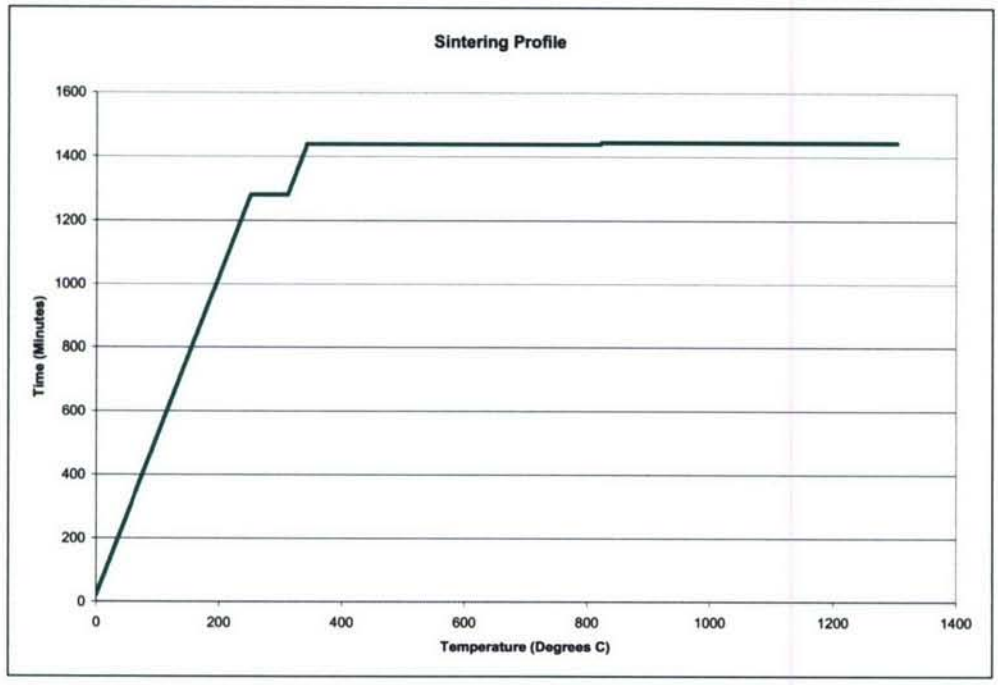

Figure 42 – Sintering Profile

Task II.4b. Sintering setup methods

Several support media were tested for the debinding and sintering cycles, including: alumina plates, molybdenum plates, and a zirconia crucible. All but the zirconia crucible resulted in either the part sticking to the support media or the part developing cracks. Debinding was best achieved in a two stage inert gas purge with the first stage comprised of 45 SCFH [Ar] + 5 SCFH [H_2] followed by 50 SCFH [Ar]. The sintering and densification cycles were best preformed in a vacuum atmosphere with long hold times at high temperatures.

Task II.4c. Sintering distortion control

Sintering distortion control will be the focus of the Year Two research and will involve the use of Finite Element Software (FE) to simulate absorbed heat and shrinkage.

III. Component Identification

Task III. 1. Component Identification

Component identification will also be the focus of the Year Two research and will include the direct involvement of personnel from the ARL.

Conclusions

Varying the powder mixture-binder-sintering profile revealed that a Ti-6Al-4V powder mixed with 3.5% CIP powder, printed with the ammonium molybdate binder, and sintered for long times at high temperature 1440 °C in vacuum produces test geometries that result in high density approaching that is needed to make functional parts by 3D dimensional printing. The iron powder induces the formation of a liquid phase that enhances the densification. The sintered microstructure shows a typical acicular structure of a-titanium with no deleterious effect of Fe visible. Further studies will include sintering distortion control with the aid of Finite Element Software (FE) to simulate absorbed heat and shrinkage. Hot isostatic pressing (HIP) will be employed in an effort to bring the titanium component to 100% density.

Acknowledgements

A special thanks goes to the Ex One Company of Irwin, Pennsylvania. Their dedicated work on re-designing a standard ProMetal R2 to safely print 3D parts using titanium-based metal powders is greatly appreciated. The technical staff at Ex One completed several hours of research involving de-binding and sintering of 3D printed titanium-based parts. A special binder developed at Ex One could be a break through for the 3D printing technology.

APPENDIX A

DIRECT METAL LASER SINTERING

Company:	ECS Gmbh, www.eos.info
Offering:	Equipment and Materials
Present Status:	Available
Number of Installations:	5 R&D, 3 Internal Service, Approx. 90 Commercial
Target Markets:	PIM, Die Casting, and Direct Parts Mfg.
Typical Tool Life (Part Quantity):	PIM: >1 Million Zinc Die Casting: >5,000 Aluminum Die Casting: >1,000
Process Style:	Direct
Key Process:	Metal Laser-Sintering
Key Process Time for 125 mm (5 inch) Cube Insert:	1 To 2 Days
Process Steps (CAD to Insert Before Water Lines):	Slice STL to Layer Data, DMLS Process, Cut Platform to Size, and Shot-Peen, and Polish If/As Necessary
Typical Delivery Time for 125 mm (5 inch) Cube Insert:	<1 Week
Raw Materials and Form:	Metal Powder Blends
Finished Tool Composite Makeup Composite Makeup:	Steel or Bronze-Based
Finished Tool Density Range:	Steel-Based up to 99.5% Bronze-Based up to 93%
Finished Tool Material Properties:	Steel-Based Comparable to Conventional Tool Steel, Bronze-Based Broadly Comparable to Aluminum
Detail Capability as Small as X mm (inch):	0.6 (0.025)
Accuracy, from CAD to Insert mm (inch):	± 0.07% + 0.05 (0.07%+ 0.002)
Surface Finish Ra μm (μin):	Up to 9 (354) as Sintered, 3 (118) after Shot-Peening
Conformal Cooling:	Channels of Unsintered Powder are Left
Multi-Material Capability:	Yes, Limited
Maximum Insert Size mm (inch):	250 x 250 x 185 (9.8 x 9.8 x 7.3)
Geometric Limitations:	Minimum Wall Thickness 0.6 mm (0.024 in.)
Cost:	$939,000 to $1,038,000

ELECTRON BEAM MELTING

Company:	Arcam AB, www.arcam.corn
Offering:	Equipment
Present Status:	Available
Number of Installations:	3 R&D, 2 Internal Service, 6 Commercial
Target Markets:	Direct Parts Mfg., PIM, and Die Casting
Typical Tool Life (Part Quantity):	PIM: >1 Million Die Casting Al Zn >100,000
Process Style:	Direct
Key Process:	Electron Beam Melting (EBM)
Key Process Time for 125 Mm (5 Inch) Cube Insert:	1 Day
Process Steps (CAD to Insert Before Water Lines):	Code, Electron Beam Melting of Powder Metal, and Conventional Finishing
Typical Delivery Time for 125 Mm (5 Inch) Cube Insert:	1 To 2 Weeks
Raw Materials and Form:	Powder Metals
Finished Tool Composite Makeup Composite Makeup:	H13 Tool Steel, Hardened
Finished Tool Density Range:	100% Dense
Finished Tool Material Properties:	Same as Conventional H13 Tool Steel
Detail Capability as Small as X mm (inch):	0.25 (0.010) (Radii Added By Hand)
Accuracy, From CAD to Insert mm (inch):	±0.3 (0.012) (Any Conventional Method Can Be Used For Further Finishing EDM, HSM, Polishing Etc)
Surface Finish Ra μm (μin):	20 To 40 (787 To 1574)
Conformal Cooling:	Yes
Multi-Material Capability:	Possible
Maximum Insert Size mm (inch):	200 x 200 x 200 (8 x 8 x 8)
Geometric Limitations:	None
Cost:	$700,000 to $1,100,000

OPTOMEC LENS

Company:	Optomec, Inc. www.optornec.corn
Offering:	Equipment
Present Status:	Available
Number of Installations:	6 R&D, 3 Internal Service, 5 Low-Volume Manufacture, 4 Repair And Overhaul
Target Markets:	PIM (Aerospace Components, Medical Device, and Defense)
Typical Tool Life (Part Quantity):	PIM >1 Million (Based On A Mold Repair Application)
Process Style:	Direct Metal Fabrication
Key Process:	Metal Deposition By Laser Engineered Net Shaping (LENS)
Key Process Time for 125 Mm (5 Inch) Cube Insert:	<1 Day (5 To 10 Hours LENS Time)
Process Steps (CAD to Insert Before Water Lines):	Load Part or Substrate, Load Slice File, Deposit Material, and Finish Machine
Typical Delivery Time for 125 Mm (5 Inch) Cube Insert:	2 To 4 Weeks
Raw Materials and Form:	Powdered Metals Including Tool Steels, Stainless Steels Including 420, Titanium, Inconel, and Others
Finished Tool Composite Makeup Composite Makeup:	Pure Metals and Alloys; Gradient Materials Structures are Optional
Finished Tool Material Properties:	99 To 100%
Detail Capability as Small as X mm (inch):	0.51 (0.020) (Off Machine, Requires Finishing)
Accuracy, from CAD to Insert mm (inch):	± 0.125 mm/25 mm (0.005 in /in.) In X (Y Requires Finishing)
Surface Finish Ra mm (min):	1 to 7.6 (200 to 300)
Conformal Cooling:	Channels Can Be Constructed or Thermally Conductive Material can be Embedded during Build
Multi-Material Capability:	Can Apply Different Metals and/or Gradient Structures with Good Control
Maximum Insert Size mm (inch):	1500 X 900 X 900 (60 X 36 X 36)
Geometric Limitations:	Lower Hemisphere of Movement
Cost:	$830,000 to $1,400,000

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